Luminescence in Crystals

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Preface

This book contains the main topics developed by the author in his lectures given in the Faculty of Science of the University of Paris. The treatment is mainly theoretical, though attention is given to the more important applications of luminescent processes, for instance, phosphors for fluorescent lamps, X-ray screens and television tubes.

This English edition is for the main part a translation of a book entitled *Luminescence Cristalline*, published by Dunod. Many additions have been incorporated, the most important being the extra chapters on electroluminescence and cathodoluminescence processes. Unfortunately the manuscript was written just before the advent of Lasers and so it has only been possible to include a few preliminary references on this item. However, a short discussion on the luminescence of ruby is included.

Professor G. F. J. Garlick has undertaken the translation and no one could be better qualified. My thanks are due to him for the translation and for many interesting discussions on the topics of the book. Professor Garlick, who acted as an impartial translator, is not responsible for my errors.

MARCH 1962   D. CURIE

Introduction

1. Luminescence

Under the general term *luminescence* we include luminous emission which is not purely thermal in origin.

According to the mode of excitation we distinguish:

– *photoluminescence* produced by absorption of light (or usually ultra-violet radiation).

– luminescence excited by accelerated particles (*cathodoluminescence* if electrons are used) or more generally by high energy radiation – X-rays or γ-rays as well as particles such as α and β particles, protons, fission fragments, &c. (*radioluminescence*). In effect, all these emissions are due to excitation by the secondary electrons produced. If the individual emissions due to single particles are considered these are known as *scintillations* and are used in the detection of the specific particles or quanta.

– *electroluminescence* produced by the application of an electric field.

– the phenomenon of *triboluminescence*, radiation being emitted by a substance subject to mechanical forces, e.g. grinding of sugar in a mortar; friction produces electrical charges and either discharges occur in the body of the material or something like electroluminescence occurs.

– *chemiluminescence* and *bioluminescence* in which emission accompanies a chemical reaction (oxidation of phosphorus in a humid atmosphere); or a biological process (glow worm: oxidation of luciferin).

The following text is confined to luminescence in crystals excluding the last group of phenomena above as well as luminescence in gases, vapours, and organic liquids or solutions.

2. Fluorescence and phosphorescence

Fig. 1 shows a typical energy-level scheme used in luminescence: the emitting system is raised by excitation from the ground state f to the excited state e; return to the ground state occurs with emission of

1

light. The emission occurs at a time t after excitation, t being the life time of the excited state and being of the order of 10^{-8} sec for atomic dipole emission; it is of the order of 10^{-5} sec in phosphorescent sulphides of the ZnS(Cu) type.
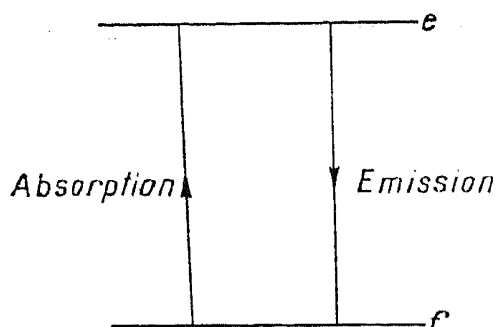
In practice, the main concern is with visible emission, but for some years studies have been made of luminescence in the ultra violet and in the infra red. Such an energy scheme applies equally well to X-rays and γ-rays; hence we speak of X-ray or γ-ray fluorescence. However, some phenomena of radiation emission (e.g. brehmsstrahlung, Cerenkov radiation) cannot be described by a diagram of the type in Fig. 1. For fluorescence the system must remain in the excited state for a time t, large compared with the frequency of the emitted radiation (Vavilov), and this is not so for such emissions. The question of their inclusion amongst luminescence phenomena has been discussed, but it is more usual to group them in another category with such phenomena as Rayleigh scattering and the Raman effect.

Fig. 1 is descriptive of *fluorescence*, the return to the ground state occurring by spontaneous emission. Fig. 2, which includes a meta-stable level m (trap or trapping state), represents the case for *phosphorescence*. The system on excitation to the state e can make a transition to the state m, which being by definition metastable does not allow of further transition $m \longrightarrow f$. Thus the system will not change from the state m unless it receives an energy E lifting it again to the excited state e. Then *phosphorescence* occurs (if there is no return to the state m, i.e. recapture into the trap) usually identical in emission with fluorescence (although the relative intensities of the various emission bands may be different), but delayed in time by an amount τ equal to the time spent in the state m.

If the energy E (usually called the trap depth) is provided by a thermal activation, then in general:

$$\frac{1}{\tau} = s \exp\left(\frac{-E}{kT}\right)$$

Fig. 1
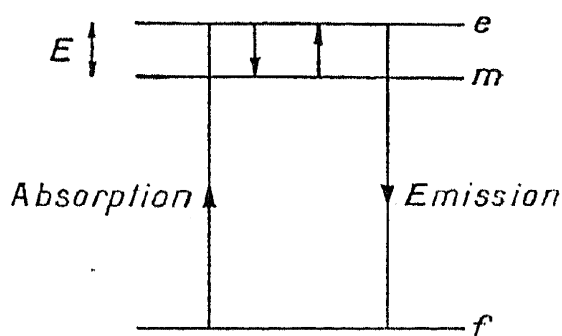
Fig. 2

where $\tau \gg t$, s is a constant, k is Boltzmann's constant, and T is the absolute temperature.

Definition due to J. and F. Perrin

'The phenomenon is fluorescence if the emission takes place by one or more spontaneous transitions.

'If, on the contrary, the emission occurs with the intervention of a metastable state followed by return to the excited state due to addition of energy, then this is phosphorescence.'

A luminescence emission with a life time of about 10^{-8} sec is indisputably fluorescence. In contrast, an effect where emission persists for the order of a second, or a longer duration, after excitation ends is almost always phosphorescence. However, in the intermediate time range, say 10^{-1} to 10^{-5} sec, it is difficult to decide between a *long fluorescence* (forbidden transition) and a *short phosphorescence* (due to very shallow traps).

A study of the variation of the luminescence decay with temperature enables the distinction to be made. The decay of fluorescence is little dependent on the temperature, but the duration of phosphorescence is strongly temperature-dependent (determined by a Boltzmann function).

The emission during excitation is often defined as fluorescence, but this is wrong in the case of a phosphorescent solid since at least a part of the emission is phosphorescence. In the case of zinc sulphides it is not certain that all electrons spend a short time in shallow traps.

The activation energy E for escape from the traps is usually provided by the thermal agitation of the environment; hence the occurrence of the Boltzmann function. However, it can also be provided by absorption of an incident photon of sufficient energy, this being known as *optical stimulation*. A burst of light is obtained when a previously excited phosphorescent solid is irradiated by light of longer wavelength than that of the excitation (usually infra-red irradiation).

3. Relation between life time τ and fluorescence efficiency η (F. Perrin)

Under certain conditions the life time τ for the fluorescence shows an appreciable dependence on temperature, the decrease in life time being accompanied by an associated fall in the fluorescence efficiency η (see Fig. 3).

The fluorescence of uranyl salts $(UO_2)^{2+}$ is due to a transition in the uranyl group, the life time being of the order of 10^{-3} sec for the non-perturbed free ion. In these brilliantly fluorescent salts, e.g. uranyl nitrate, the life time $\tau \approx 10^{-3}$ sec is usually found to depend very little on temperature and the quantum yield of fluorescence is of the order of 100 per cent. In contrast in other salts such as $RbUO_2(CH_3CO_2)_3$, τ is much smaller and temperature-dependent.
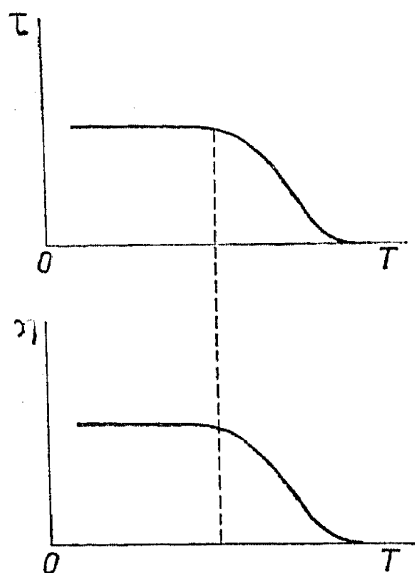
At 4°K $\tau \approx 1780$ μsec, at 293°K $\tau \approx 57$ μsec and the efficiency is very small (Hall and Dieke). This effect is, however, never of the same order as those observed in phosphorescence for the trapping life times. For the traps giving the visible phosphorescence of zinc sulphide (ZnS–Cu) with $E = 0.65$ eV and $s \approx 10^9$ sec^{-1}, the trapping occurs for 3 min at ordinary temperatures and for 1,600 days at -100°C and $\tau \approx 10^{800}$ sec at 4°K, if it is sensible to extrapolate a formula to such proportions.

Fig. 3

The explanation lies in a competition between radiative transitions with a probability p_r depending little on temperature and non-radiative transitions ('de-excitation' of the material by thermal agitation) having a probablity p_{nr} increasing with temperature.

The normal life time of the fluorescence will be $1/p_r$, but the observed life time is given by

$$\frac{1}{\tau} = p_r + p_{nr}$$

If there are no non-radiative transitions at zero temperature the life time is

$$\frac{1}{\tau_{(0)}} = p_r$$

and so

$$\eta_{(T)} = \frac{\tau_{(T)}}{\tau_{(0)}} = \frac{p_r}{p_r + p_{nr}}$$

In general, radiative and non-radiative transitions compete even at absolute zero, and so we have the characteristic fluorescence relation

$$\frac{\tau_{(T)}}{\tau_{(0)}} = \frac{\eta_{(T)}}{\eta_{(0)}}$$

In phosphorescence the introduction of non-radiative transitions usually shortens the decay time, but a simple relation such as the above is not found.

The phenomenon was first studied by Perrin in organic fluorescent solutions and later by Kröger and Hoogenstraaten for willemite (Zn_2SiO_4–Mn), &c.

4. Centres and traps in the different classes of phosphorescent solids

The crystals of phosphorescent solids known as 'conventional' are not photoluminescent in the pure state: the luminescence is due to the addition of a *luminogen* or *activator* in the form of a trace impurity. For example, in phosphorescent sulphides, copper, manganese, bismuth, &c. – ZnS(Cu), CaS(Bi) or ZnS:Cu, CaS:Bi, &c. In some cases *crystal lattice defects* provide localized levels, like those of impurities, which play the part of the activator.

The exceptions, that is, crystals which show photoluminescence in the pure state, are materials containing groups which function like foreign molecules in the matrix crystal from which they are separated by screening (J. T. Randall). For example, in uranyl salts such as $(NO_3)_2UO_2$, nH_2O, the UO_2^{2+} group responsible for luminescence behaves as a separate molecule surrounded by a shield due to the water molecules of hydration. The luminescence disappears on heating but reappears when water is reintroduced. Certain rare earth salts are luminescent (Eu, Gd, Sm, Tb, Dy), due to transitions of the internal 4f electrons. In these cases the crystalline state is not necessary for luminescence and it is observed when the ions are in solution or *in vitreo*.

Leaving aside these exceptions, we have introduced two kinds of states involved in luminescence:

 – *luminescence centres* which contain levels responsible for the luminescence emission spectrum.

 – *electron traps* responsible for the phosphorescence or persistence of emission after cessation of excitation.

We follow Mott in distinguishing two main groups of luminescent solids:

A. *The cases where the emitting system is quasi-atomic* (*crystals often known as non-photoconductors*). This does not mean that photoconductivity cannot be excited by absorption of radiation of suitable

wavelength, but that under the usual conditions of luminescence excitation the photoconductivity is negligible and it is not necessary to raise electrons into the conduction band in order to produce luminescence.
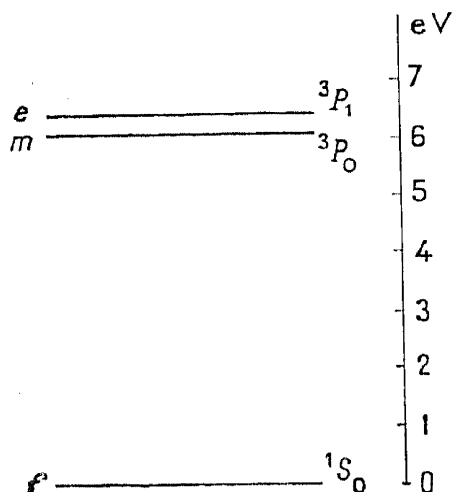
The typical solid of this class is KCl(Tl), the system responsible for luminescence being to a first approximation the Tl^+ ion. The levels denoted by f, m and e of Fig. 2 are applicable to this ion (Fig. 4). The scheme used in this case is thus identical with that of Jablonski for organic molecules and dyes.

Fig. 4

The heavy atoms Hg, Tl^+, Pb^{2+}, Bi^{3+} belong to this class and are iso-electronic with Tl^+, i.e. they have the same set of electronic energy levels.

The homogeneous series of ions:

$$Ga^+ Ge^{2+} \ldots In^+ Sn^{2+}$$

may also be added to this class (Tech. B. Louchtchik and co-workers).

B. *Photoconducting, phosphorescent crystals* typical of which are ZnS(Cu), ZnS(Ag), CdS(Ag), &c. Excitation raises electrons from the valence band or from the luminescence centres into the conduction band of the crystal (which is thus also a semiconductor). There thus arises a marked photoconductivity showing strong correlation with the luminescence.

Between the valence and conduction bands we have to introduce and consider the recombination centres, donor levels, and electron traps. The distinction between luminescence centres and traps is less easy than in the case of *quasi-atomic systems*, but in practice an energy level can be put in one or other of these classes.
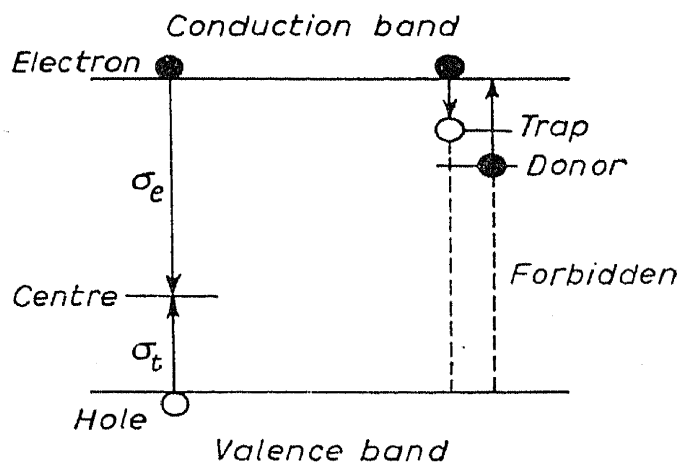
Fig. 5

(*a*) The recombination centres for electrons and holes are characterized by an effective cross-section σ_e for electron capture and σ_t for

hole capture, which if not of the same order of magnitude are at least both of the same importance.

A centre is a luminescence centre if the probability of radiative emission p_r is much greater than that for non-radiative emission p_{nr}:

i.e.
$$p_r \gg p_{nr}$$

which is the case for Cu centres in ZnS.

A centre is a '*killer*' centre if, on the contrary,

$$p_r \ll p_{nr}$$

which is the case for Fe, Ni and Co in ZnS. Their introduction in large quantities results in a 'poisoning' of the luminescence.

(*b*) Electron traps and electron donors show a large capture probability for conduction electrons, but transitions from them to the valence band are almost forbidden:

i.e.
$$\sigma_e \gg \sigma_t$$

If the level is normally empty (available for electron capture) it constitutes an *electron trap*, if normally occupied it is a *donor level*.

(*c*) Hole traps and acceptor levels can be defined in the inverse sense to the cases of electron traps and donor levels:

i.e.
$$\sigma_t \gg \sigma_e$$

If a level is normally unoccupied by holes it is a hole trap, and if it is empty of electrons and ready to capture a valence band electron it is an acceptor level.

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† A general bibliography on books and comprehensive reviews on luminescence is given at the end of the book (page 325).
We have not attempted to give an exhaustive list of references: this would be beyond the scope of this book. We have quoted some of the most important papers relative to each problem treated in the text; we hope that it will be sufficient as a first step in establishing the relevant bibliography.

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Classification of the different localized levels in the forbidden gap, traps, centres, etc. ...

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WILLIAMS, F. E. (1960) 'Irreversible thermodynamics of solid state luminescence', Spring Meeting, Electrochemical Society, Chicago, May 1-5.

Angular distribution of fluorescent brightness

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Dipole and Quadrupole Radiation:

Probabilities of Emission and Absorption

We shall not give here the general theory for the phenomena of emission and absorption of radiation. The reader may refer to more specific writings for this, for example:

E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press);

W. Heitler, *The Quantum Theory of Radiation* (Oxford, Clarendon Press).

We have made considerable use of the following:

F. Perrin, *Emission de rayonnement par les atomes et les noyaux* (Cours du Collège de France, 1950-1-2);

A. Berthelot, *Les champs multipolaires en électromagnétisme*;

unfortunately the last two have not been published.

Only the elementary results for dipole and quadrupole radiations are necessary in considering luminescence. Effectively the emission probability for the various multipole orders falls by a factor $\approx (a/\lambda)^2$ each time the order l changes by unity, a being the source dimension and λ the wavelength of the emitted radiation.

For visible luminescence ($\lambda \approx 5,000$ Å) from atoms ($a \approx 1$ Å) the factor a/λ is thus 1/5000, and so quadrupole radiations are very feeble compared with dipole radiations and higher-order emissions are almost negligible. An electric dipole transition will have, for example, a life time of 10^{-8} to 10^{-7} sec, a magnetic dipole transition 10^{-3} to 10^{-1} sec, and a quadrupole transition an even longer life time.

(In luminescent materials the interaction of the emitting atom with the crystal lattice can usually cause an appreciable reduction in these values.)

In contrast for hard X-rays ($\lambda \approx 10^{-1}$ Å and $a \approx 10^{-10}$ cm, the size of the inner shells of heavy atom) the same factor a/λ can reach

1/10; similarly for γ-ray conditions multipole radiations are no longer negligible.

I. DIPOLE AND QUADRUPOLE MOMENTS

1. Electrostatic potential due to a charge distribution

An atom, molecule or luminescence centre is composed of one or more nuclei surrounded by a certain number of negatively charged electrons. These form an assembly of charges e; at points $\delta_i(x_i, y_i, z_i)$. We now find the potential due to this system at a point $P(X, Y, Z)$ at a distance R from the origin of coordinates:

$$V = \sum \frac{e_i}{r_i}$$

r_i being the distance from P to the charge e_i.

Assuming R to be large compared with the distances of the charges from the origin, a Taylor series can be developed:

$$V = \frac{1}{R}\Sigma e_i + \sum \frac{\partial(1/R)}{\partial X}\Sigma e_i x_i + \frac{1}{2}\sum \frac{\partial^2(1/R)}{\partial X \partial Y}\Sigma e_i x_i y_i + \ldots$$

This indicates the total charge of the distribution Σe_i, the *vector dipole moment* μ which by definition has components

$$\mu_x = \Sigma e_i x_i \ldots$$

and the *tensor quadrupole moment*

$$B^{(2)} = \begin{pmatrix} B_{xx} & B_{xy} & B_{xz} \\ B_{yx} & B_{yy} & B_{yz} \\ B_{zx} & B_{zy} & B_{zz} \end{pmatrix}$$

a symmetric tensor of the second order (six separate components) given by

$$B_{xx} = \Sigma e_i x_i^2 \qquad B_{xy} = \Sigma e_i x_i y_i \ldots$$

In general we have a series of polar moments 2^l and each one characterized by a tensor

$$B^{(l)} = \Sigma e_i [\delta_i]^l$$

and contributing to the total potential of the system the contracted product

$$V_l = \frac{1}{l!}\left[\text{grad}_0^{(l)}\left(\frac{1}{R}\right) . B^{(l)} \right]$$

$\text{grad}_0^{(l)}$ denoting the tensor of the partial derivatives of order l of $1/R$ calculated at the origin.

The similarity will be noted between the definition of dipole moment and that of the centre of gravity of a collection of masses

and also between the quadrupole moments and moments of inertia. By a suitable choice of axes of reference it is possible to diagonalize the tensor $B^{(2)}$ in the same way as the tensor formed by the moments and products of inertia.

2. Potentials due to dipoles and quadrupoles

A dipole formed by charges A and B equal to $+e$ and $-e$ has a moment

$$\mu = eBA$$

and gives rise to a potential which at large distances away, say ten times the length of the dipole, reduces to a term involving $1/R^2$:

$$V_1 = \frac{\mu \cos \theta}{R^2} = \frac{(\mathbf{n} . \mu)}{R^2}$$

$\mathbf{n}$ being a unit vector in the direction $\mathbf{R}$.
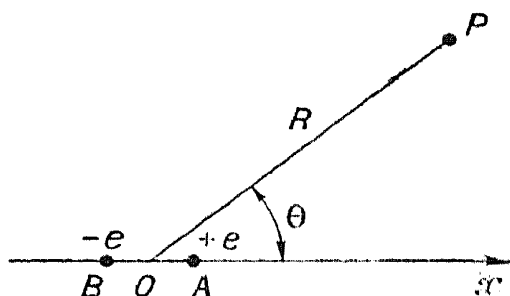
Fig. I.1 *Electrostatic dipole*

The potential is zero along the axis for $\theta = \pi/2$, but not so the field which is thus transverse; the field is radial about the axis of the dipole, ($\theta = 0$).

A quadrupole is formed by two equal and opposed dipoles, displaced from each other, say four charges $ABCD$ of $+e$, $-e$, $+e$, $-e$ arranged at the corners of a parallelogram. This gives rise to a potential:

$$V_2 = \tfrac{1}{2} \operatorname{grad}_0^{(2)}(1/R) . B^{(2)}$$

Using the two *invariants* attached to the tensor $B^{(2)}$, we know[†] its trace:

$$B = B_{xx} + B_{yy} + B_{zz}$$

and the quadratic form:

$$B(X, Y, Z) = B_{xx}X^2 + \ldots + 2B_{yz}YZ + \ldots$$

† In the analogy between the tensor of the moments and products of inertia the invariant B corresponds to the moment of inertia with respect to the origin such that $B(X,Y,Z)$ is the quadratic form appearing in the definition of the ellipsoid of inertia.

We can then obtain explicitly the derivatives which occur in $\mathrm{grad}_0^{(2)}$:

$$V_2 = \frac{1}{2}\frac{1}{R^3}\left[3\frac{B(X,Y,Z)}{R^2} - B\right]$$

The anisotropy of a quadrupole is more complex than that of a dipole and depends on the type of quadrupole involved.
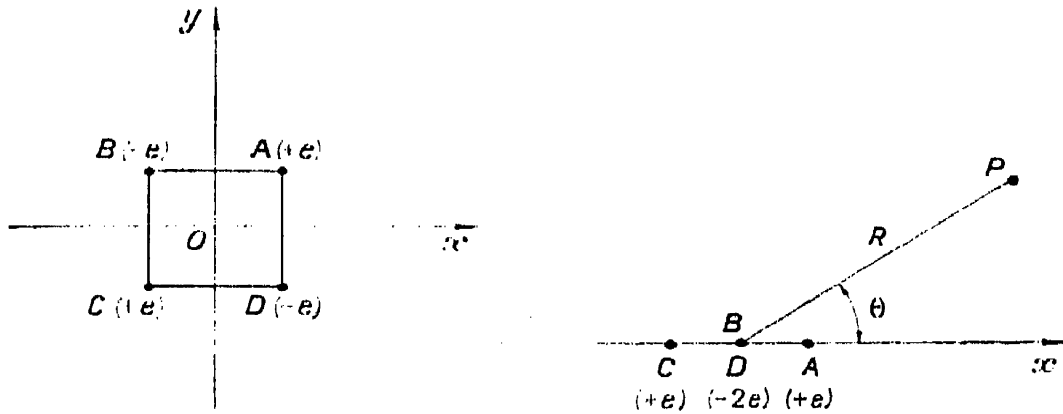
Fig. I.2 *Two types of quadrupoles*

Consider first the case where the four charges A, B, C, and D are arranged at the corners of a square. The only non-zero component of the tensor $B^{(2)}$ is then $B_{xy} = e(AB)^2$, from which

$$V_2 = \frac{3e(AB)^2\cos\theta\sin\theta}{R^3}$$

The potential and the field are both zero along the axis Oz normal to the plane of the quadrupole. To diagonalize $B^{(2)}$ it is sufficient here to take the axes at 45° to the previous ones.

When the four charges A, B, C, D are aligned along the same axis they form an *axial quadrupole*. The only non-zero component is then $B_{xx} = 2e(AB)^2$.

$$V_2 = \frac{2e(AB)^2}{R^3}\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)$$

We see the appearance of the Legendre polynomial $P_2(\cos\theta)$. In a more general way, for an axial multiple of order 2^l formed by charges of alternate sign with equal distances between them, the number of charges at each point being equal to the successive coefficients in the binomial expansion, the potential is given by

$$V_l = \frac{l!\,e(AB)^l}{R^{l+1}}P_l(\cos\theta)$$

3. Development of potential due to a multipole in spherical harmonics

Any '2^l-pole' is equivalent to the sum of 2^l axial multipoles of the same order arranged along the ray vectors of the poles. This enables us to expand the potential V_l of the 2^l-pole in the following form:

$$V_l = \frac{1}{R^{l+1}} \sum_{m=-l}^{m=l} a_l^m Y_l^m(\theta, \phi)$$

We use for this the expansion of the Legendre polynomial for the Y_l^m's:

$$P_l(\cos \alpha) = \frac{4\pi}{2l+1} \sum_{m=-l}^{m=l} Y_l^m(\theta, \phi) Y_l^m(\theta', \phi')$$

where θ and ϕ are the polar coordinates of the direction $\mathbf{R}$, and θ' and ϕ' the polar coordinates for the direction of the e_ith charge, α being the angle between these two directions. By integration over a volume element dv of the charge system we obtain the value of the coefficient a_l^m.

$$a_l^m = \frac{4\pi}{2l+1} Q_l^m, \qquad Q_l^m = \int \delta^l Y_l^m(\theta', \phi') \rho \, dv$$

where $\rho(\delta)$ is the charge density. Q_l^m is termed the *multipole electric moment of order l, m*. $2l+1$ coefficients are necessary to define the 2^l-poles in place of the $\frac{1}{2}(l+1)(l+2)$ coefficients of the tensor $B^{(l)}$. This is because the coefficients are not independent, the resultant potential V having to satisfy Laplace's equation as well as its derivatives.

In particular the moment

$$Q_2^0 = \sqrt{\tfrac{5}{16}\pi} . Q$$

where
$$Q = \int \delta^2 (3\cos^2 \theta - 1) \rho \, dv$$

and defines the quadrupole moment of a distribution formed by rotation about the axis $\theta = 0$.

II. DIPOLE AND QUADRUPOLE RADIATION IN ELECTROMAGNETISM

1. Maxwell's equations

Consider an electromagnetic field *in vacuo* due to a charge distribution of density ρ and a current distribution of density $\mathbf{j}$. This field is

defined by the electric field **E** and the magnetic field **H** related by the equations

$$\text{curl } \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t} \text{ (law of induction)}$$

$$\text{div } \mathbf{D} = 4\pi\rho \text{ (Gauss's theorem)}$$

$$\text{curl } \mathbf{H} = \frac{1}{c}\frac{\partial \mathbf{D}}{\partial t} + 4\pi\mathbf{j} \text{ (Ampère's theorem)}$$

$$\text{div } \mathbf{B} = 0 \text{ (i.e. no free magnetic poles)}$$

The system of units is defined by

$$\varepsilon_0 = \mu_0 = 1$$

Unless otherwise indicated, magnetic quantities and also **j** are given in e.m.u and electrostatic quantities in e.s.u. Since a vacuum is assumed:

$$\mathbf{D} = \mathbf{E} \quad \text{and} \quad \mathbf{B} = \mathbf{H}$$

From these relations one obtains the law of charge conservation:

$$\text{div } \mathbf{j} + \frac{1}{c}\frac{\partial \rho}{\partial t} = 0$$

The fields **E** and **H** can be expressed in terms of a scalar potential Φ and a vector potential **A** by the relations

$$\mathbf{E} = -\text{grad } \Phi - \frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} \quad \text{and} \quad \mathbf{H} = \text{curl } \mathbf{A}$$

When the potentials are chosen so that they satisfy the Lorentz condition

$$\text{div } \mathbf{A} + \frac{1}{c}\frac{\partial \Phi}{\partial t} = 0$$

Φ and **A** are solutions of

$$\Box\Phi = 4\pi\rho \qquad \Box\mathbf{A} = 4\pi\mathbf{j}$$

Where $\Box$ is the d'Alembertian

$$\Box = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}$$

2. Solution of Maxwell's equations by the retarded potential method

Consider a distribution of moving charges $\rho(x,y,z)$ and $\mathbf{j}(x,y,z)$ occupying a region around the origin of coordinates. We now consider the potential at $P(X,Y,Z)$ at a distance **R** from the origin and **r** from the charge (x,y,z).

When P is outside the charge distribution we obtain the following:

$$\Phi(X,Y,Z,t) = \int\int\int \rho\frac{(x,y,z,t-r/c)}{r}\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$$

$$A(X,Y,Z,t) = \int\int\int \mathbf{j}\frac{(x,y,z,t-r/c)}{r}\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$$

the integral extending over the whole volume occupied by the charges.

The retardation r/c represents the time for electromagnetic waves of velocity c to reach the point P after emission by the charge at
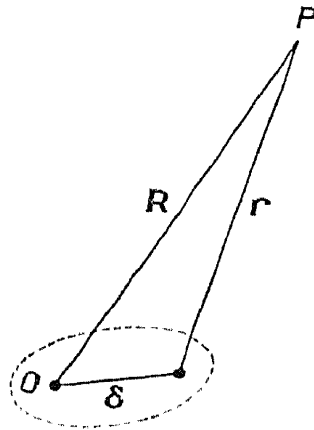
Fig. I.3 *Potential produced by a moving charge*

(x,y,z). These expressions satisfy the equations for Φ and A (involving the d'Alembertian) as well as the Lorentz condition resulting from the conservation of charge.

3. Systems in harmonic vibration

If r is the vibrational frequency then we can write

$$\rho = \rho_0\, e^{2\pi i\nu t}, \qquad \mathbf{j} = \mathbf{j}_0\, e^{2\pi i\nu t}$$

implying of course the real parts of these expressions. We also introduce the wavelength $\lambda = c/v$, the reduced wavelength $\lambdabar = \lambda/2\pi$ and the reduced wave number

$$k = \frac{2\pi\nu}{c} = \frac{1}{\lambdabar}$$

Then we have

$$\rho = \rho_0\, e^{ikct}; \qquad \mathbf{j} = \mathbf{j}_0\, e^{ikct}$$

and charge conservation requires that:

$$\mathrm{div}\,\mathbf{j}_0 + ik\rho_0 = 0$$

Using these notations, the retarded potential formulae become

$$\Phi = \Phi_0\, e^{ikct}, \qquad A = A_0\, e^{ikct}$$

$$\Phi = \iiint \rho_0 \cdot \frac{e^{-ikr}}{r} \, dv$$

$$A_0 = \iiint j_0 \frac{e^{-ikr}}{r} \, dv$$

4. Potential distribution among successive multipole orders

The potential formula for Φ_0 differs from that for the electrostatic potential V for the charge distribution ρ_0 by the replacement of $1/r$ by

$$f(r) = \frac{e^{-ikr}}{r}$$

The exponential takes account of the different retardations between the different point charges of the system. Analogous to the development of V in para. I.1, Φ_0 can be given as follows:

$$\Phi_0 = f(R) \iiint \rho_0 \, dv + \sum_{l=1} \frac{1}{l!} (\mathrm{grad}_0^{(l)} f(R) \cdot B_0^{(l)})$$

the derivatives of $f(R)$ being taken at the origin. Each component of A_0 can be obtained in a similar way.

Charge conservation during vibration requires that

$$\iiint \rho_0 \, dv = 0$$

We then obtain the results for successive multipole orders (l), taking together the $(l+1)$th term of Φ_0 and the lth term of A_0.

Electric dipole radiation

We take the first non-zero term of each series and obtain

$$\Phi_0 = \mathrm{grad}_0 f(R) \cdot \mu_0 = -\mathrm{grad}_P f(R) \cdot \mu_0$$

$$A_0 = f(R) \iiint j_0 \, dv$$

μ_0 is the vector dipole moment

$$\mu_0 = \iiint \rho_0 \delta \, dv$$

δ being the radial vector for a point charge (x,y,z) of the source.

Charge conservation gives:

$$\iiint \mathbf{j}_0 \, dv = ik\mu_0$$

so that the potentials finally depend only on the quantity μ_0.

We now introduce $f(R)$ and its derivative $f'(R)$

$$f(R) = \frac{e^{-ikR}}{R}; \qquad f'(R) = -\frac{1+ikR}{R}f(R)$$

so that we can now write

$$\Phi_0 = -(\mathbf{n}.\mu_0)f'(R)$$
$$\mathbf{A}_0 = ik\mu_0 f(R)$$

For small distances, i.e. small compared with $\lambda(kR \ll 1)$ but large compared with the size of the source, we can put $f(R) \approx 1/R$: thus we obtain the electric field due to a stationary dipole of moment μ_0 and the magnetic field due to the current $\mathbf{j}_0$.

At large distances $(kR \gg 1)$ $f'(R)$ reduces to $-ikf(R)$, which gives terms in $1/R$ in the potentials as well as in the fields, i.e. we have the radiation fields. We find

$$\mathbf{H} = k^2(\mathbf{n} \wedge \mu_0)\frac{e^{-ikR}}{R} e^{2\pi i \nu t}$$

$$\mathbf{E} = -k^2[\mathbf{n} \wedge (\mathbf{n} \wedge \mu_0)]\frac{e^{-ikR}}{R} e^{2\pi i \nu t}$$

where $\mathbf{n}$ is the unit vector in the direction $\mathbf{R}$.

These solutions are for divergent waves and this arises from the use of the retardation potentials.

We see that

$$\mathbf{E} = \mathbf{H} \wedge \mathbf{n}$$

(E and H have the same magnitude and are both transverse.) The radiation energy is equal to the flux of the Poynting vector:

$$\mathbf{S} = \frac{c}{4\pi}(\mathbf{E} \wedge \mathbf{H})$$

and integrating over all space

$$W = \frac{16\pi^4\nu^4}{3c^3}|\mu_0|^2$$

where W is the energy radiated per second.

The dipole μ_0 can be realized by assuming a point charge in harmonic oscillation. Knowing the oscillator energy and comparing this to W, we can deduce the mean life time

$$\tau = \frac{3mc^3}{8\pi^2e^2\nu^2}$$

For $\lambda \approx 6{,}000$ Å we obtain

$$\tau \approx 1 \cdot 6 \times 10^{-8} \text{ sec}$$

Anisotropy of the emission

If the moment μ_0 is real this corresponds to the case of a point charge oscillating along a direction which we take as the polar axis O_z. If θ is the angle between the direction OP and this axis, the emission per unit solid angle is dependent on $\sin^2 \theta$ (this is seen straight away

Linear oscillator · Circular oscillator
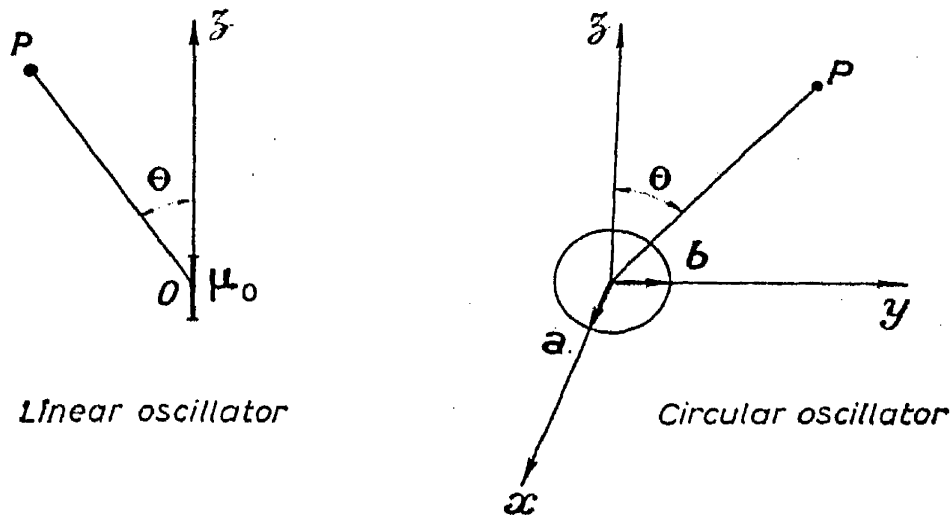
Fig. I.4 *Anisotropy of emission for dipole oscillators*

in the expression for H, knowing that the radiant energy varies as the square of the field).

The emission is zero along the dipole axis. However, the electrostatic field is a maximum (but radial for reasons of symmetry: there could not be a radiation field because this must be transverse).

The angular distribution of the radiation field is identical with that of the transverse component of the electrostatic field but differs from that of the total electrostatic field.

In general $\mu_0 = a + ib$ and is complex. This corresponds to the case of the elliptical oscillator. In particular, if $a = b$ the oscillator is circular and the anisotropy of the emission depends on $1 + \cos^2 \theta$.

Case of a zero dipole moment

The same approximation as above can be used in the derivation of the potentials, i.e. we take the first non-zero term.

Consider first of all the scalar potential

$$\Phi_0 = \tfrac{1}{2}(\mathrm{grad}_0^{(2)} f(R) \cdot B_0^{(2)})$$

$B^{(2)}$ being the tensor quadrupole moment. Thus to describe Φ_0 it is not necessary to introduce any new quantities; as in the electrostatic case it is sufficient to replace $1/R$ by $f(R) = e^{-ikR}/R$.

However, it is necessary for the vector potential to introduce new parameters related to the charge distribution. If δ is the radius vector of a point (x,y,z) of the source

$$\mathbf{A}_0 = -f'(R) \int\int\int (\mathbf{n}.\delta)\mathbf{j}_0 \, dv$$

We can establish that

$$\int\int\int xj_{0x} \, dv = \tfrac{1}{2}ik \int\int\int \rho_0 x^2 \, dv = \tfrac{1}{2}ikB_{0xx}$$

$$\int\int\int yj_{0z} \, dv = \tfrac{1}{2}ik \int\int\int \rho_0 yz \, dv + \tfrac{1}{2}\int\int\int (yj_{0z} - zj_{0y}) \, dv$$

$$= \tfrac{1}{2}ikB_{0yz} + M_{0x}$$

We are thus led to introduce in addition to $B_0^{(2)}$ the magnetic dipole moment $\mathbf{M}_0$

$$\mathbf{M}_0 = \tfrac{1}{2} \int\int\int (\delta \wedge \mathbf{j}_0) \, dv$$

When only the magnetic moment is involved we have a magnetic dipole wave emission for which

$$\Phi_0 = 0, \qquad \mathbf{A}_0 = -f'(R)(\mathbf{M}_0 \wedge \mathbf{n})$$

Although these potentials are very different from those obtained for the electric dipole radiation, the fields can be obtained by a simple permutation of $\mathbf{E}$ and $\mathbf{H}$ (and of course replacement of μ_0 by $\mathbf{M}_0$).

The radiation energy is thus

$$W = \frac{16\pi^4 \nu^4}{3c^3} |\mathbf{M}_0|^2$$

The magnetic dipole moment is of the order of a Bohr magneton

$$M_0 \approx \frac{eh}{4\pi mc}$$

while $\mu_0 \approx ea_0$, where a_0 is the Bohr atomic radius

$$a_0 = \frac{h^2}{4\pi^2 me^2}$$

We can deduce that M_0/μ_0 is of the order of the fine structure constant

$$\frac{M_0}{\mu_0} \approx \frac{\pi e^2}{hc} = \frac{1}{2} \cdot \frac{1}{137}$$

which gives a much smaller probability of magnetic dipole emission than of electric dipole emission in the ratio $1:10^5$ (and still 100 times weaker if the radiation comes from an intercombination transition).

When M_0 is zero but $B_0^{(2)}$ is not, we have the case of electric quadrupole emission for which we have already noted the expression for Φ_0 while
$$A_{0x} = -f'(R)\tfrac{1}{2}ik(\mathbf{n}.B_0^{(2)})_x$$
From these formulae the fields can be deduced. We shall not derive these but simply remark that at large distances they are again transverse and satisfy the relation
$$\mathbf{E} = \mathbf{H} \wedge \mathbf{n}$$
this applying to all multipole orders.

The emitted radiation has the value
$$W = \frac{8\pi^6\nu^6}{15c^5}\left\{\sum \mid B_{yy} - B_{zz}\mid^2 + 6\sum \mid B_{yz}\mid^2\right\}$$
If a is the source dimension, the quadrupole moment is of the order of ea^2 while the electric dipole moment is $\approx ea$, the coefficient is on the other hand multiplied by ν^2/c^2 and the emission probability is thus multiplied by $\approx (a/\lambda)^2$, which is of the order of 10^{-7} or 10^{-8}.

We can also write W as follows:
$$W = \frac{8\pi^6\nu^6}{5c^5}\mid Q\mid^2$$
$\mid Q\mid^2$ representing the expression
$$\mid B_{xx} - \tfrac{1}{3}B\mid^2 + \mid B_{yy} - \tfrac{1}{3}B\mid^2 + \mid B_{zz} - \tfrac{1}{3}B\mid^2 + 2(\mid B_{xy}\mid^2 + \mid B_{yz}\mid^2 + \mid B_{zx}\mid^2)$$
or in the most condensed form
$$Q = B^{(2)} - BI$$
B being the trace of the tensor $B^{(2)}$ and I the unit diagonal tensor.

Reference may be made to J. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics* (Wiley, New York, 1952), p. 586, for a study of the emission anisotropy for different multipole orders Q_l^m. We only note here that the angular distribution of the radiation energy for the real axial quadrupole, oscillating linearly along the OZ axis, depends on $\cos^2\theta \sin^2\theta$.

III. PROBABILITIES OF RADIATIVE ABSORPTION AND EMISSION

1. The Hamiltonian of the particle (electron of mass m and charge $-e$, e being taken positive) in an electromagnetic field Φ, $\mathbf{A}$ is given in

B

non-relativistic classical mechanics by

$$\mathbf{H} = \frac{1}{2m}\mathbf{P}^2 - e\Phi$$

$$\mathbf{P} = mv = \mathbf{p} + \frac{e}{c}\mathbf{A}$$

where $\mathbf{P}$ is the kinetic momentum, $\mathbf{p}$ the total momentum (that of particle and field). Neglecting the terms in $(eA/c)^2$, these equations give

$$H = \frac{1}{2m}\mathbf{p}^2 - e\Phi + \frac{e}{mc}(\mathbf{p}\cdot\mathbf{A})$$

The term $(eA/c)^2$ is a relativistic term and we shall neglect it. The Hamiltonian is separable into

$$H_{\text{particle}} = \frac{1}{2m}\mathbf{p}^2 - e\Phi$$

giving the electron motion in the field derived from the electrostatic potential Φ and

$$H_{\text{interaction}} = \frac{e}{mc}(\mathbf{p}\cdot\mathbf{A})$$

In quantum mechanics $\mathbf{p}$ must be replaced by the operator

$$\mathbf{p} = \frac{\hbar}{i}\nabla$$

where ∇ is the operator gradient. However, $\mathbf{p}$ and $\mathbf{A}$ are non-commutative and we have

$$\nabla\cdot\mathbf{A} = \mathbf{A}\cdot\nabla + \text{div }\mathbf{A}$$

It is also convenient to choose a potential scale so that the scalar potential Φ is zero for the radiation field (in contrast to previous condition imposed by using retarded potentials). We know that the physical results should be independent of the scale chosen for the potentials. The Lorentz condition implies that div $\mathbf{A} = 0$ and the difficulty of the non-commutative operators disappears. We then have

$$H_{\text{interaction (radiation-electron)}} = \frac{e}{mc}\frac{\hbar}{i}(\mathbf{A}\cdot\mathbf{grad})$$

2. The transition probability

This interaction introduces simultaneous transitions between electron states and the photons of the radiation field. *The transition probability per unit time* is

$$P = \frac{4\pi^2}{h}\left|\int\Psi^*_{\text{final}}H_{\text{interaction}}\Psi_{\text{initial}}\,d\tau\right|^2\rho(E)$$

where $\rho(E)$ is the density of oscillator states around the energy $E = h\nu$ for the photons

$$\rho(E)\, dE = V\frac{8\pi\nu^2}{c^3}\, d\nu$$

(normalized to the volume V).

The Ψ functions can be resolved into a $\psi(r)$ function of the electron coordinates multiplied by a product of the eigen functions of the oscillator for the photon field. The matrix elements for the latter are classical. We give here only the results of these calculations.

When the vector potential **A** is assumed constant at all points in the charge source, matrix elements appear of the form

$$\frac{\hbar}{i}\int \psi_f{}^* \mathbf{grad}\ \psi\ d\tau = m\frac{d}{dt}\int \psi_f{}^*\mathbf{r}\psi_i\, d\tau$$

(a formula which when $\psi_i = \psi_f$ reduces to $p = mv$ for the movement of the centre of gravity).

We also obtain the matrix elements for the electric dipole moment:

$$\mu_{if} = e\mathbf{r}_{if}, \qquad \mathbf{r}_{if} = \int \psi_f{}^*\mathbf{r}\psi_i\, d\tau$$

We then have for the probability per second of emission:

$$P_{\text{emiss.}} = (N+1)\frac{64\pi^4\nu^3}{3hc^3}\,|\,\mu_{if}\,|^2$$

N being the mean number of photons in the energy $h\nu$ (if $N = 0$ we have spontaneous emission) and for the probability of absorption per second

$$P_{\text{abs.}} = N.\frac{64\pi^4\nu^3}{3hc^3}\,|\,\mu_{if}\,|^2$$

The luminous emission intensity per second from an atomic emitter (photon energy $E = h\nu$ multiplied by the transition probability) is

$$I(h\nu) = \frac{64\pi^4\nu^4}{3c^3}\,|\,\mu_{if}\,|^2$$

The effective absorption cross-section is by definition

$$\sigma(\nu) = \frac{\text{No. of transitions per atom per sec}}{\text{No. of incident photons per cm}^2\text{ per sec}}$$

The numerator is $P_{\text{abs.}}$ and the denominator is the photon flux per second

$$= cN\frac{8\pi\nu^2}{c^3}\, d\nu$$

From which

$$\sigma(\nu) = N\frac{64\pi^4\nu^3}{3hc^3} \mid \mu_{if} \mid^2 \frac{c^3}{cN8\pi\nu^2 \, d\nu}$$

We thus obtain the effective cross-section integrated over an assembly of 'physically identical' states (that is, with the same matrix element μ_{if}) in practice over all the possible neighbouring energies to $h\nu$ for the absorbed photons:

$$\int \sigma(\nu) \, d\nu = \frac{8\pi^3\nu}{3hc} \mid \mu_{if} \mid^2$$

One often considers:

$$\int \sigma(E) \, dE = \frac{8\pi^3\nu}{3c} \mid \mu_{if} \mid^2$$

The *absorption coefficient* $k(E)$ cm^{-1} is given by the product of the effective cross-section $\sigma(E)$ and the concentration of absorbing atoms.

These classical formulae are for atoms *in vacuo*. We shall see later how they may be transformed for the case of absorbing or emitting atoms in a crystalline medium of refractive index n. However, the formulae above suffice for the study of emitted and absorbed radiation as a function of the factor $\mid \mu \mid^2$, and we only need to introduce a coefficient which takes account of the refractive index n when considering the absolute intensity of the radiation (Smakula formula).

Compare the quantum expression giving $I(h\nu)$ above and the preceding formula from classical electromagnetism for the radiated energy (*correspondence principle*)

$$W = \frac{16\pi^4\nu^4}{3c^3} \mid \mu_0 \mid^2$$

We see that the quantum formula differs from the classical one in that we replace the dipole moment μ_0 by the matrix element of the dipole moment for the transition. If we do this we have to include a factor of 2 in the matrix element and of 4 in the transition probability. The factor 2 can be explained as follows:

The correspondence principle establishes in a general way a relation between the intensity at the harmonic of frequency ν in the frequency spectrum and the radiated energy in the quantum theory due to photons of energy $h\nu$. However, classically we do not distinguish between ν and $-\nu$, that is, between photons emitted and photons absorbed. In applying the correspondence principle to

$$\mu_0 = e\int \rho\mathbf{r} \, d\tau$$

the density ρ must be replaced not by $\psi_f \psi_i$; which gives

$$\mu_{if} = e \int \psi_f{}^* \mathbf{r} \psi_i \, d\tau$$

but by the symmetrical expression $\psi_f \psi_i + \psi_i \psi_f$, and we must take the real part

$$\text{Re} \, (\psi_f{}^* \psi_i + \psi_i{}^* \psi_f) = 2 \, \text{Re} \, (\psi_f{}^* \psi_i)$$

which explains the correspondence

$$\mu_0 \longrightarrow 2\mu_{if}$$

3. Magnetic dipole and electric quadrupole radiation

The same correspondence occurs in the expressions for emission and absorption of magnetic dipole and electric quadrupole character.

In the magnetic dipole case the luminous intensity emitted at frequency ν is

$$I(h\nu) = \frac{64\pi^4 \nu^4}{3c^3} \mid \mathbf{M}_{if} \mid^2$$

and the integrated absorption cross-section is

$$\int \sigma(E) \, dE = \frac{8\pi^3 \nu}{3c} \mid \mathbf{M}_{if} \mid^2$$

In the case of electric quadrupole radiation (which is obtained when we introduce the first derivative of $\mathbf{A}$ (the first derivative of the retardation e^{-1kr} between different points of the charge source in the classical case) we obtain

$$I(h\nu) = \frac{32\pi^6 \nu^6}{5c^5} \mid Q_{if} \mid^2$$

$$\int \sigma(E) \, dE = \frac{4\pi^5 \nu^4}{5c^3} \mid Q_{if} \mid^2$$

We refer back to the expression developed for Q at the end of paragraph II in which each component B_{xx}, B_{xy} ... of the tensor $B^{(2)}$ can be replaced by the matrix element of the same quantity for the transition $i \longrightarrow f$.

4. Selection rules

The selection rules are most easily appreciated by resolution of the dipole and quadrupole potentials, &c., into spherical harmonics dependent on Q_l^m (para. I.3) with $m = -l, -l+1 \ldots l-1 +l$. We can show that radiation of multipole order l, m has a total angular

momentum l for which the O_z component is m (m units of $h/2\pi$). Thus for the emitting atoms the angular momentum

$$\mathbf{J}_i = \mathbf{J}_f + 1$$

and for the O_z component

$$M_i = M_f + m$$

Since there is no multiple radiation for $l = 0$, all radiative transitions $J_i = 0 \longrightarrow J_f = 0$ are forbidden in all multipole orders.

For $l = 1$ (dipole case) we have

$$\Delta J = 0, \pm 1, \qquad \Delta M = 0, \pm 1$$

giving an electric dipole wave if there is a change of parity for the wave function ψ (Laporte's rule) and a magnetic dipole wave if the parity does not change (given the parities of the operators μ and $\mathbf{M}$).

For $l = 2$

$$\Delta J = 0, \pm 1, \pm 2; \qquad \Delta M = 0, \pm 1, \pm 2$$

giving an electric quadrupole wave if there is no change in parity.

For $\Delta J = \pm 2$, only quadrupole or higher order radiation is allowed. For $\Delta J = 0$ ($0 \longleftrightarrow 0$ excluded) or ± 1, we have an electric dipole wave if the parity changes and a mixture of electric quadrupole and magnetic dipole waves if there is no change in parity. The magnetic dipole radiation will usually predominate since its probability is only 10^{-5} times less than that for electric dipole radiation, while that for electric quadrupole radiation is about 10^{-8} times less.

Forbiddenness of intercombination radiation. The operators μ, $\mathbf{M}$ and $B^{(2)}$ are symmetrical to the exchange of two electrons. If, for example, we consider a system of two electrons, the transition from a triplet state (spatial wave function antisymmetric with respect to the exchange) to a singlet state (spatial wave function symmetrical) is forbidden.

The spin-orbit interaction partially lifts the forbiddenness. In an average atom, an intercombination transition will be 100 times weaker than an allowed transition of the same multipole order. In heavy atoms such as Hg, Tl$^+$, &c., this factor is reduced to about 10.

'Spin-flip' transitions. Chromium as an activator. In an allowed transition the electronic configuration changes by means of an electron transition from one 'orbit' to another. There are some transitions for which the configuration does not change, being the same in the ground and excited states. These states differ only by the 'turning

over' of one electron spin. In luminescence the question arises in the case of ruby (aluminium oxide containing Cr_2O_3):

The emission spectra of chromium-activated phosphors are quite different from the spectra of other phosphors, and to some extent they can be compared to the spectra of rare earths. They consist of a red fluorescence which may be resolved into a large number of narrow lines; among them there is a characteristic intense doublet (Deutschbein). In ruby, the position of this doublet is, at 20°C, at

$$R_1 : 6{,}942 \cdot 3 \text{ Å, } (14{,}404 \text{ cm}^{-1})$$
$$R_2 : 6{,}927 \cdot 4 \text{ Å, } (14{,}435 \text{ cm}^{-1})$$

These lines are slightly displaced when the temperature is varied, but
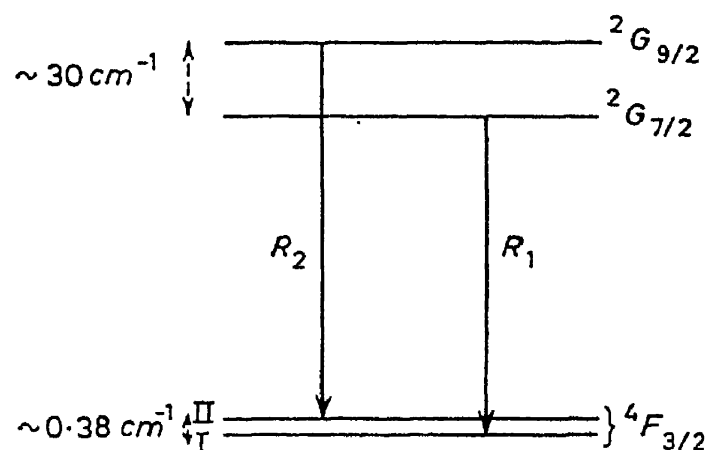
Fig. I.5 *Energy-levels scheme for the emission spectrum of the main lines R_1, R_2 in ruby*

the main effect is an exponential dependence of the relative intensities:

$$\frac{I(R_2)}{I(R_1)} = \exp\left(-\frac{W}{kT}\right) \qquad W \approx 29 \cdot 2 \text{ cm}^{-1}$$

Chromium is incorporated as Cr^{3+}. In the fundamental level $^4F_{3/2}$, the spins of the three outer 3d electrons are parallel; in the excited $^2G_{7/2}$ and $^2G_{9/2}$ levels, one of the valence electrons is anti-parallel to the other.

In addition, when the Cr^{3+} ion is incorporated into the crystal, the fundamental level is split into 2 twofold, orbitally degenerate states, I and II, and 3 single states (not shown on the Fig. I.5). The value of the splitting between I and II is accurately known from micro-wave absorption measurements: it corresponds to a frequency of 11,593 Mc/s.

It may be noted that this splitting is small compared with the

energy difference between states of different J values: thus the degeneracy of the levels of the free Cr^{3+} ion is raised by the crystal field, but the mixing of these levels is probably quite negligible for the most important low energy levels, occurring in the red R-emission of ruby. A discussion, using as a starting-point the terms derived for the free ion, as it was attempted by Deutschbein, Thosar and Pringsheim, is thus not too inaccurate.†

A spin-flip transition is also assumed for the case of the activator manganese. Sometimes, this activator is embedded as Mn^{4+}, which is isoelectronic with Cr^{3+}, and an emission results which contains several lines, also situated in the red part of the spectrum. This is the case for magnesium germanate, $Mg_2GeO_4(Mn)$, and magnesium oxide, $MgO(Mn)$, phosphors, but more often one has to deal with Mn^{2+} ions, with five outer 3d electrons: such is the case for $ZnS(Mn)$, $Zn_2SiO_4(Mn)$, &c. . . . We shall discuss these phosphors in Chapter V (page 122).

Such transitions are naturally forbidden for an electric dipole approximation. They comprise various radiations, some of electric quadrupole and others principally of magnetic dipole character. Their mean life time is rather long (5 msec in ruby) and very sensitive to crystal lattice interactions.

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† The level scheme which is proposed here differs slightly from the generally accepted scheme due to Sugano and Tanabe (1958). The fundamental level and the excited level involved in the R-emission of ruby derive respectively from ^4F and ^2G states; the difference is in part a matter of notation.

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Emission and Absorption Spectra and the Configurational Coordinate Model (Example of Thallium Activated Alkali Halides)

Luminescence spectra differ from atomic spectra in two basic aspects:

(*a*) Bands (of the order of hundreds of ångströms wide) rather than lines are generally observed. Exceptions are the Ewles–Kröger luminescence and exciton emission.

(*b*) The emitted radiation is displaced to longer wavelengths compared to the absorbed radiation (Stokes's Law). More specifically, the band maxima for emission and absorption are displaced but it is possible to have an overlap of the long wavelength side of the absorption band and the short wavelength side of the emission band.

The above phenomena are due to the interaction between the emission centre and the crystal lattice which can be treated by means of the configurational coordinate model. This model is particularly appropriate for the case of a quasi-atomic emission system; the interaction can be represented in a most satisfactory way by using a single configurational coordinate to give the distance between the luminescent ion and its nearest neighbours in the surrounding lattice. As an example we take the case of thallium activated potassium chloride KCl(Tl) which has been extensively studied, in particular by F. Seitz and by F. E. Williams. The model can also be applied to cases where the centres are less localized, in particular to luminescent semiconductors although the configurational coordinate cannot be given such a specific interpretation as in the above case.

I. STRUCTURE OF A 'NON-PHOTOCONDUCTING' LUMINESCENT SOLID: KCl(Tl)

In general, KCl(Tl) is prepared by incorporation of 1 part per 10,000 to 1 part per 100 TlCl in KCl. Two intense absorption bands due to Tl$^+$ ions are found at 1,960 and 2,500 Å respectively, with a weaker band at about 2,100 Å. Excitation is usually effected in the 2,500 Å band (mercury radiation is at 2,537 Å). An intense ultra-violet emission occurs at 3,050 Å and also a blue emission at 4,750 Å to 4,900 Å.
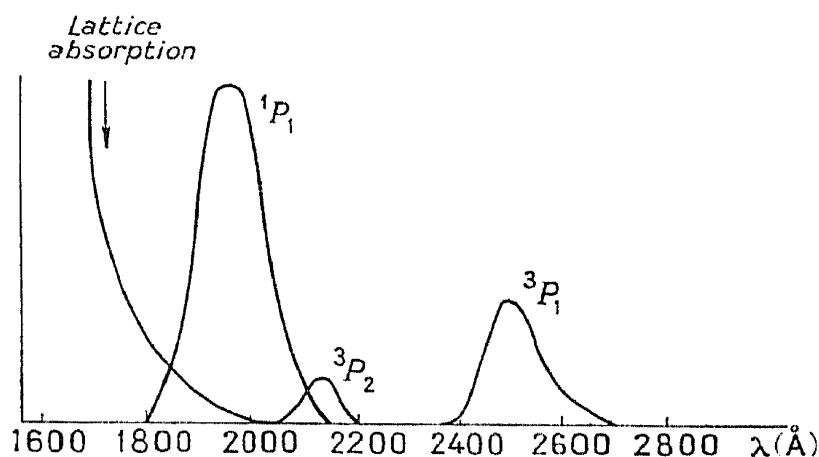
Fig. II.1 *Absorption spectra of KCl(Tl)*
(After Seitz)

1. Energy levels in the matrix lattice of KCl

The valence band (or filled band) is assumed to be due to the Cl$^-$ ions. The conduction band (normally empty) is ascribed to levels of the neutral K atoms. The transition of an electron from valence band to conduction band corresponds to its migration from the valence shell of the Cl$^-$ ion to the outer shell of a K$^+$ ion which thus becomes a neutral atom.

The energetic positions of the bands relative to the zero of potential (electron taken to infinity outside the crystal) are described by the values χ and ψ respectively (see Fig. II.2):

χ is the electronic affinity of the solid: it is the work obtained in taking an electron from infinity to the bottom of the conduction band of the crystal.

ψ is the separation or extraction energy: it is the work done in removing an electron from the top of the valence band to an infinite distance outside the crystal.

$h\nu = \psi - \chi$ is the width of the forbidden energy gap.

Mott and Gurney have developed a method of calculating ψ and χ by considering the energy balance in a cycle which for ψ consists of removing the Cl^- ion from the crystal in order to remove its electron
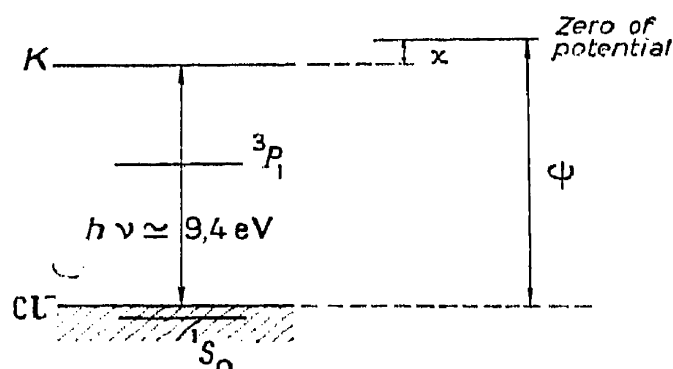
Fig. II.2 *Energy levels in KCl(Tl). The filled band due to the K^+ ions is situated below the valence band*

and then putting it back into the crystal. For χ a K^+ ion is removed in order to add an electron to it and then it is also put back into the crystal. This enables ψ and χ to be determined from the electron affinity of chlorine and the ionization potential of free K atoms which are known from experiment.

The result is

$$\psi \approx 9 \cdot 5 \text{ eV} \quad \text{and} \quad \chi \approx 0 \cdot 1 \text{ eV}$$

and so

$$h\nu = \psi - \chi = 9 \cdot 4 \text{ eV}$$

which corresponds to a long wavelength absorption limit of $1,310 \text{ Å}$.

2. Energy levels of the free thallium ion

The ground state of the Tl^+ ion is an ^1S state (a central core outside which are two $6s$ electrons ($6s^2$). The first excited state is a P state ($6s\,6p$). From Hund's rule we assume that the lowest state of the $6s\,6p$ configuration is a triplet state ^3P at a lower energetic position than the singlet ^1P because of the sign of the exchange integral (the inverse is true for nuclear spectra using the model of M. Mayer). The effect of spin-orbit interaction is to lift the degeneracy of the triplet state, the state with the lowest J value being the least altered, i.e. the electron spin being anti-parallel to the orbital moment. The energy level scheme of Fig. II.3 is obtained, the energy values given there being from experiment.

Seitz and Williams associate the observed absorption bands for Tl^+ ions in the crystal with the following transitions:

$$1,960 \text{ Å} \qquad ^1S_0 \longrightarrow \, ^1P_1 \qquad (f \approx 1)$$
$$2,100 \text{ Å} \qquad ^1S_0 \longrightarrow \, ^3P_2 \qquad \text{(very weak)}$$
$$2,500 \text{ Å} \qquad ^1S_0 \longrightarrow \, ^3P_1 \qquad (f \approx 0\cdot 1)$$

The transition $^1S_0 \longrightarrow \, ^3P_1$ being a singlet to triplet state transition will be forbidden if the coupling is purely of Russell–Saunders type: spin-orbital interaction is considered as a very weak perturbation.†
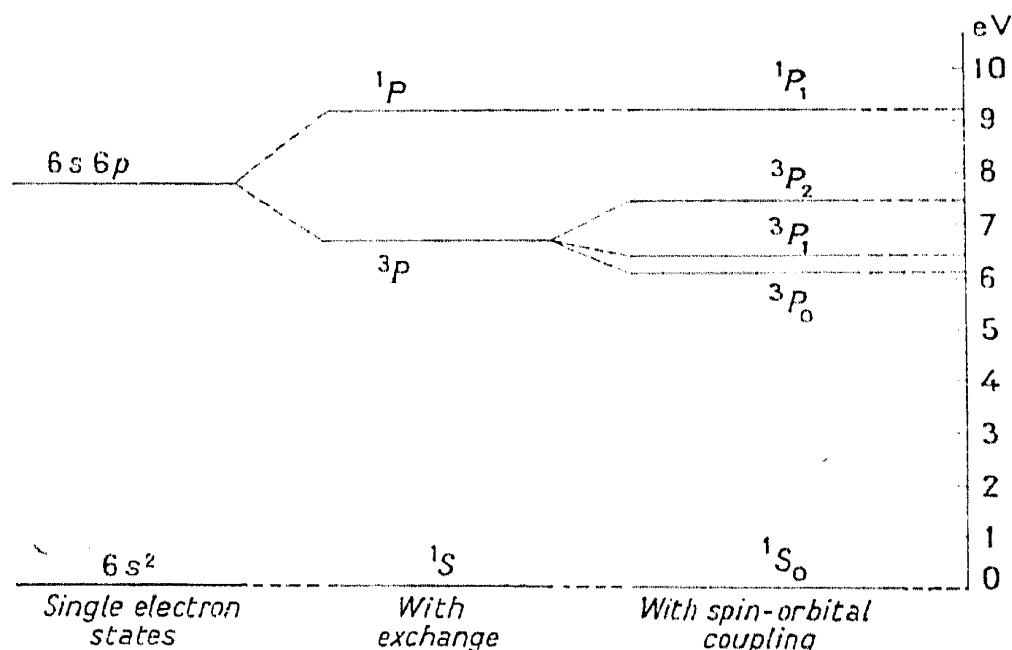
Fig. II.3 *Energy levels of the free Tl^+ ion*

Actually, in heavy atoms it is allowed‡ with an oscillator strength (f) less than that for the transition $^1S_0 \longrightarrow \, ^1P_1$ which indicates partial **jj** coupling. The ratio of oscillator strengths will be about 30 for the free Tl^+ ion: (the intercombination transition is relatively enhanced in the crystal). The mercury line at 2,537 Å used for excitation in this band ($^1S_0 \longrightarrow ^3P_1$) is due to a transition between the same spectroscopic states $^3P_1 \longrightarrow \, ^1S_0$ (Hg and Tl^+ have the same electronic structure).

† It will be remembered that in Russell–Saunders coupling – or L.S coupling – the orbital moments l couple to give a resultant L and the spins s to give a resultant S and only then is spin-orbital coupling introduced to give J = L+S.

This is only valid for weak spin-orbital coupling: if the coupling is strong, then l and s for each electron are coupled (j = l+s) and the various j's are then added, this being known as **jj** coupling.

‡ The transition life time is of the order of 10^{-7} sec and so the use of thallium activated alkali halides as scintillators gives a shorter life time than that of photoconducting phosphors of the ZnS type (10^{-5} to 10^{-4} sec).

The transition $^1S_0 \longrightarrow {}^3P_0$ is forbidden for all orders ($J = 0$ to $J = 0$) the $^3P_0$ level constituting a typical *electron trap*.

The transition $^1S_0 \longrightarrow {}^3P_2$ is also forbidden but only for a dipole approximation: the level $^3P_2$ also forms an electron trap. These transitions cease to be forbidden when the Tl^+ ion is perturbed by a neighbouring Tl^+ ion which occurs at higher concentrations.

3. Location of the ground state $^1S_0$ of Tl^+ in the energy band scheme of KCl

F. E. Williams has calculated the ionization energy of Tl^+ in the crystal:

$$Tl^+ \longrightarrow Tl^{2+} + \text{conduction electron}$$

Outside the crystal this ionization:

$$Tl^+ \longrightarrow Tl^{2+} + \text{free electron}$$
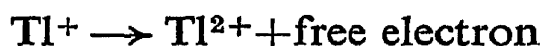
requires an energy I equal to the second ionization potential of thallium, i.e. $I = 20 \cdot 3$ eV.

However, inside the crystal the replacement of Tl^+ by Tl^{2+} yields the energy $\alpha e^2/d$ and is 8 eV (α is the Madelung constant, d the interatomic distance). This value is only a first approximation and must be modified to take account of the different polarizabilities of the lattice ions.

We obtain the energy χ in taking an electron from infinity into the conduction band. From this calculation the ground state for thallium is found to be

$$I - \frac{\alpha e^2}{d} - \chi = 12 \text{ eV}$$

below the conduction band: polarization terms reduce this to $9 \cdot 5$ eV.

The ground state of the Tl^+ ion is thus $0 \cdot 1$ eV below the top of the valence band. Since 2,500 Å corresponds to a quantum of about 5 eV, the $^3P_1$ excited state in KCl(Tl) is situated at $9 \cdot 5 - 5 = 4 \cdot 5$ eV below the conduction band.

It is this which determines the quasi-atomic nature of the emission transitions in the phosphor. Excitation with 2,500 Å radiation can excite the Tl^+ centre without ionizing it: in addition, the energy of $4 \cdot 5$ eV cannot be provided by thermal ionization. However, at high intensities the 2,500 Å can ionize certain Tl^+ ions already excited by a first quantum: this is stepwise excitation of an electron from valence to conduction band. Besides, KCl can have other levels than those of the Tl^+ ions (due to F centres, pairs of Tl^+ ions, &c.), some of

which can be ionized giving a very small probability of a weak photo-conductivity (thus the term non-photoconducting was placed in inverted commas in the title). However, this photoconductivity is not necessary in the production of emission; in fact, it perturbs the luminescence kinetics, the freed electrons being able to recombine with emission centres for intense excitation and for high thallium concentration (Antonov–Romanovsky). Such a recombination results in the same emission bands as for direct excitation of the activator ion (Tech. B. Louchtchik and co-workers); but the filling of traps will be different. Traps not connected with the thallium centres will now contribute to the phosphorescence decay. The same kind of phenomena appear under X-ray or vacuum ultra-violet excitation.

II. ABSORPTION AND EMISSION PHENOMENA IN KCl(Tl), THE CONFIGURATIONAL COORDINATE DIAGRAM (Mott and Seitz)

1. Introduction to the model

To account for the difference in emission and absorption wavelengths:

$$^1S_0 \longrightarrow\ ^3P_1 \text{ (absorption)} \qquad \lambda = 2{,}500 \text{ Å}$$
$$^3P_1 \longrightarrow\ ^1S_0 \text{ (emission)} \qquad \lambda = 3{,}050 \text{ Å}$$

as well as the width of the emission and absorption bands:

$$E \text{ at half height} = \begin{matrix} 0\cdot3 \text{ eV for absorption} \\ 0\cdot6 \text{ eV for emission} \end{matrix}$$

(values at ordinary temperatures: the values are reduced by one-half at 80°K) we must introduce the interaction between the thallium ion Tl^+ and the remainder of the crystal.

To a first approximation we consider the Tl^+ ion substituted for a K^+ ion, the six neighbouring Cl^- ions vibrating about the Tl^+ ion. We consider only the vibrational mode in which the same distance r between the Cl^- and Tl^+ ions occurs for all Cl^- ions. The state of the system formed by the Cl^- ions interacting with the Tl^+ ion can be characterized by the distance r called the *configurational coordinate*.

To a second degree of approximation we must also introduce the interaction of the six Cl^- ions with the six nearest K^+ ions of the lattice situated on the same radius vector at a distance r' from the Cl^- ions. This leads clearly to a re-definition of the configurational coordinate.

The configurational curve or diagram is that which defines the potential energy $U(r)$ of the system Tl^+ plus lattice as a function of the coordinate r. Two curves must be considered: that for the ground state $\mathscr{U}^g$ (Tl^+ in $^1S_0$ state) and that for the excited state of the Tl^+ ions ($^3P_1$).

It is rarely possible to give such a precise physical meaning to the coordinate r and moreover to be able to calculate the configurational curves. F. E. Williams was able to obtain both for KCl(Tl)
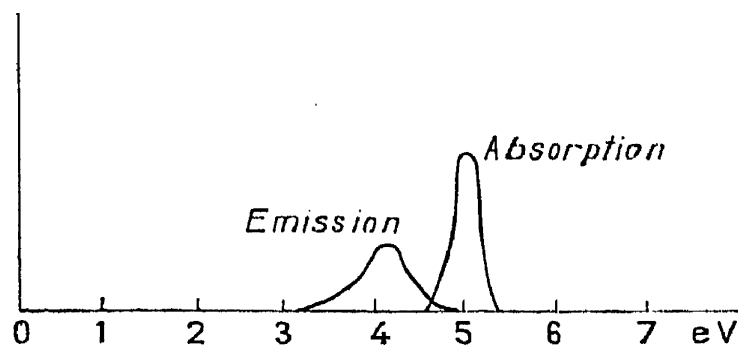
Fig. II.4 *Absorption and emission spectra of KCl(Tl). Experimental results at room temperature*

and this is why it was chosen as an example. Generally, the best one can do is to show that a system of configurational curves can be drawn to represent the experimental results. In several cases, however, these curves, once derived experimentally, can be used to predict new phenomena, e.g. F centre luminescence. We shall examine the latter later.

In the case of KCl(Tl) Williams uses the Hartree functions for Cl^- and K^+ and calculates those for Tl^+. The value of these functions has since been criticized, in particular by Knox and Dexter, but nevertheless the results obtained are still in good agreement with the facts.

2. The interaction between Tl^+ and Cl^-

This includes – a Madelung electrostatic term E_M,
   – an exchange repulsion term E_R,
   – a Van der Waals attraction term E_{vW},
   – a correction to the preceding term for the attraction between the dipoles induced on the Cl^- ions by the perturbation of the lattice resulting from introduction of the thallium E_I,
   – for the excited state a correction E_C to the electrostatic energy due to overlap of the charge distributions around the different ions.

We thus have for the ground state:

$$\mathscr{U}^g = E_R + E_{vW} + E_M + E_I$$

and for the excited state:

$$\mathscr{U}^e = E'_R + E'_{vW} + E'_m + E'_I + E_C + 6{\cdot}5 \text{ eV}$$

$6{\cdot}5$ eV being the difference in the electronic energies of the two states in the free thallium ion.

It is the correction E_C to the Madelung electrostatic energy due to overlap of the charge distributions of the Tl^+ and Cl^- ions (overlap which is much larger in the excited state) which is responsible for the greater part of the change in the equilibrium position of the ions according to the particular electronic state of the thallium ion and thus for the Stokes separation between the absorption and emission bands.

In the perfect KCl lattice the distance of the K^+ ion from its nearest Cl^- ion neighbour is $r_0 = 3{\cdot}14$ Å in equilibrium. At this distance from the nucleus the normal charge density of the $6s$ electron of Tl^+ is only $0{\cdot}01$, while that of the $6p$ electron is about $0{\cdot}05$ according to Williams's calculations. The overlap of the chlorine and thallium ions is thus effectively more important when the latter is in the excited P state than when it is in the ground state S. E_C added only to the excited state energy is actually the difference in the overlap coulomb energies of the two states.

The electrostatic attraction between the Tl^+ and Cl^- ions is the resultant of the mutual coulomb repulsion of the nuclei, of the surrounding electrons and of the attraction of the surrounding electrons of one nucleus for the other nucleus. The correction E_C is the sum of several terms of opposite sign but finally it results from the diminution in the repulsion of the two electron clouds. We consider an external layer of the thallium ion. The part of the chlorine electron cloud it includes is not repulsed but is subject to a null effect. Therefore the attraction between chlorine and thallium ions with partial electronic overlap is greater than that for the net charge e of each concentrated at the centre of each respective ion.

As a consequence *the distance r between the chlorine and thallium ions in equilibrium is about 0·3 Å smaller in the excited state than in the ground state.*

After E_C the most important terms are E_R the exchange repulsion and E_{vW} the Van der Waals attraction. E_C varies more rapidly with r

than E_vW but less rapidly than E_R. It follows that the curve $\mathcal{U}^e(r)$ is less sharp than $\mathcal{U}^g(r)$, corresponding to a smaller vibrational quantum for the ions when the thallium is in the excited state.

The calculation of the energies $\mathcal{U}^g(r)$ and $\mathcal{U}^e(r)$ is first made for the second neighbour K^+ ions held in their equilibrium positions in the perfect KCl lattice while the different displacements of the Cl^- ions occur ($\Delta r = r - r_0$). The energies $\mathcal{U}$ are thus sensibly quadratic functions of Δr:

$$\mathcal{U}^{e,g}(\Delta r) = a^{e,g}(\Delta r - \Delta r_0)^2 + \text{constant}$$

Δr_0 is the displacement of Cl^- ions from equilibrium positions in the perfect lattice when a K^+ ion is replaced by a Tl^+ luminescence centre.

The same calculation is then made for the displacement $\Delta r'$ of the second neighbour K^+ ions from their normal position in the perfect KCl lattice. The energies $\mathcal{U}$ can then be represented by quadratic functions of Δr and $\Delta r'$ with coefficients assigned to them by the method of least squares:

$$\mathcal{U}^{e,g}(\Delta r, \Delta r') = A^{e,g}(\Delta r - \Delta r_0)^2 + B(\Delta r' - \Delta r_0')^2 + \text{constant}$$

These six K^+ ions are displaced $\Delta r'$ from their equilibrium position $\Delta r_0'$ by the introduction of the Tl^+ ion into the lattice. The coefficients A are obviously different from the a's.

It would be most accurate to use the two coordinates Δr and $\Delta r'$. However, in order to have only one configurational coordinate, Williams now assumes that for each Δr value the remainder of the lattice has the equilibrium value $\Delta r' = \Delta r_0'$. The energies $\mathcal{U}$ are then only functions of Δr:

$$\mathcal{U}^{e,g}(\Delta r) = A^{e,g}(\Delta r - \Delta r_0)^2 + \text{constant}$$

as shown in Fig. II.5.

It is clear that such a simple approach is only justified if the influence of the displacements $\Delta r'$ of the second neighbours is small. The perturbation resulting from $\Delta r' \neq 0$ is no more than a tenth of an electron volt. If the correction due to second neighbours had been large, then account would have had to be taken of the third neighbour effects, and so on. Each time a new definition of the configurational coordinate Δr would have had to be made.

We thus see that this model is particularly appropriate to calculations for very *localized centres* such as Tl^+ in KCl. For extensive centres such as boron acceptors in silicon† it is better to use a model

† Corresponding to absorption bands at about 0·04 eV.

developed by various authors (Huang and Rhys, Pekar, Meyer, &c.) in which a direct treatment of the interaction between the centre and phonons of the perfect crystal is made, without giving special significance to the coordinates of specific atoms in the crystal. The results obtained by these two approaches are often very similar.
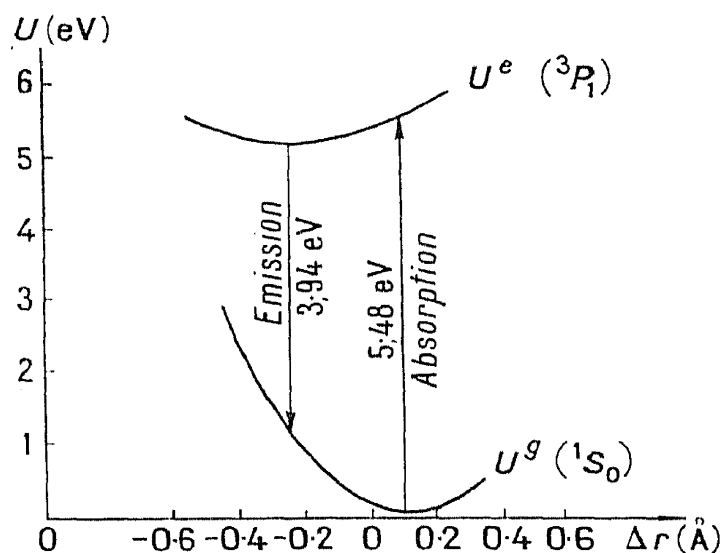
Fig. II.5 *Configurational coordinate diagram for KCl(Tl)*
(*After Williams, 1951*)

Δr is the displacement of the neighbouring Cl^- ions from their mean positions in the perfect KCl lattice

For luminescence where the centres are quite localized, more or less as in KCl(Tl), the configurational coordinate model is generally preferable, but with Lax we believe it is not always necessary to attribute to the oscillators with energies $\mathcal{U}^g$ and $\mathcal{U}^e$ the nature of vibrating ions. Sometimes as a first approximation it may be possible to introduce only one configurational coordinate r, which can be described by a complicated function of the coordinates r_n of several ions in the crystal:

$$r = f(r_1, r_2, \ldots r_n)$$

However, even if r exists, it will not be a linear function of the coordinates r_n. From a theoretical aspect (see page 52) the general situation is that a configurational coordinate scheme is a convenient representation of the absorption and emission characteristics over not too large a temperature range, but for large ranges the parameters such as ionic mass and oscillator frequencies must be modified. Experimental accuracy has not yet revealed such variations.

3. Position of the absorption and emission band maxima

In the diagram of Fig. II.5 we obtain the mean frequencies of absorption and emission ν_0 by using the vertical transitions $h\nu_0$ (Franck–Condon principle) from the minimum of the curve $\mathscr{U}^g(r)$ of the ground state for absorption and from the minimum of the excited state curve $\mathscr{U}^e$ for the emission.

Thus for absorption

$^1S_0 \longrightarrow {}^3P_1$; $\;h\nu_0 = 5\cdot48$ eV calculated (Fig. II.5) compared with 5·0 eV in experiment (Fig. II.4)

and for emission

$^3P_1 \longrightarrow {}^1S_0$; $\;h\nu_0 = 3\cdot9$ eV calculated and 4·06 eV experimental.

The vibrational quantum of the ground state is $h\nu_g = 0\cdot016$ eV and that of the excited state $h\nu_e = 0\cdot01$ eV. The mean number of vibrational quanta thermally emitted after absorption in order for the system to fall into the minimum of $\mathscr{U}^e$ is $S_a = 41$, while after luminescence emission the number emitted to return to the minimum of $\mathscr{U}^g$ is $S_e = 67$.

The calculation described above is that made initially by F. E. Williams (1951). Since this time, many improvements in the theory have been suggested by different workers, chiefly the re-normalization of the wave function for the thallous ions in the excited p-state, when these ions are introduced into the crystal, and the modification of the spin-orbit coupling affecting the separation between the ^1P and ^3P states. These corrections are extremely sensitive to crystalline interactions. Configurational curves much more intricate than the curves of Fig. II.5 have thus been proposed, including a pronounced mixing of singlet and triplet states. However, it is worthy of note that the last paper by Johnson and Williams (1960) comes back again towards the simplicity of the initial model. The configuration curve for the ground state $^1S_0$ remains unchanged, but the $^3P_1$ curve suffers slight changes, and the agreement with experiment is better.
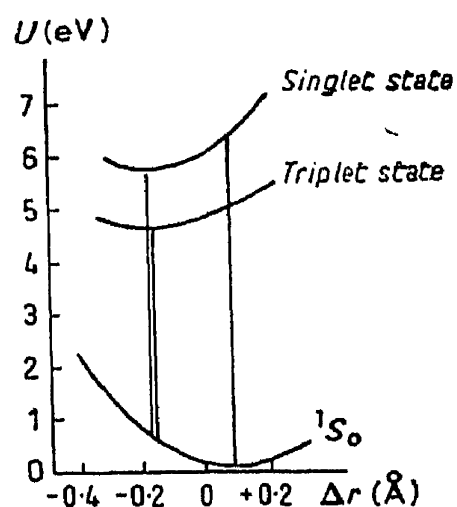
Fig. II.6 *New, simplified configuration model for $^1S_0$, $^3P_1$ and $^1P_1$ states in KCl(Tl)* (*Johnson and Williams, 1960*)

Another fundamental calculation, i.e. using also the wave functions of Tl$^+$ ions as starting-point, has been made by Kristoffel (1959). The same ground state $^1S_0$ and emitting level $^3P_1$ are considered, and in the same way as in Johnson and Williams's calculations, but only the totally symmetric vibrations of the Cl$^-$ ions are considered. However, the choice of the wave functions for the *p*-state is slightly different and takes into account their angular dependence. This calculation leads to a smaller displacement of the ions than in the Johnson and Williams theory. The agreement with experiment is a little better than in the Williams calculation of 1951 but not so good as in the Johnson and Williams model of 1960. However, for these three calculations this agreement is as good as it may reasonably be hoped to be from theories using only one configurational co-ordinate.

TABLE II.1

Comparison between the numerical values of the ionic vibrational quanta hv$_f$ and hv$_e$, and the displacements of the ions r$_0$, for the three theories described in the text above

	hv_f	hv_e	r_0
Williams, 1951	0·016 eV	0·010 eV	0·30 Å
Johnson and Williams, 1960	0·016 eV	0·012 eV	0·26 Å
Kristoffel, 1959	0·019 eV	0·015 eV	0·16 Å

Other absorption and emission bands in KCl(Tl)

While the 2,500-Å absorption band is described as due to the $^1S_0 \longrightarrow {}^3P_1$ intercombination transition, the intense absorption band at 1,960 Å is connected with the allowed $^1S_0 \longrightarrow {}^1P_1$ transition (page 34). In addition to the 3,050 Å-emission ($^3P_1 \longrightarrow {}^1S_0$), a blue emission is observed in the region 4,750–4,900 Å.

In the initial Williams theory, this blue emission was ascribed to the $^1P_1 \longrightarrow {}^1S_0$ transition. Thus the long-wave emission band was associated with the short-wave absorption band. This huge Stokes shift might be explained by assuming a much larger change in the equilibrium configuration of the ions for the $^1P_1$ state ($r_0 \approx 0.5$ Å) than for the $^3P_1$ state, but no fundamental calculation had then been made on this point.

The state of affairs is now more satisfactory since the recent discovery, by Eby and Teegarden and by Johnson and Williams, of a

new emission band centred at 2,470 Å; this band is excited by irradiation in the 1,960-Å absorption band. Thus the postulated scheme is now the following:

2,500 Å absorption	$^1S_0 \longrightarrow {}^3P_1$
3,050 Å emission	$^3P_1 \longrightarrow {}^1S_0$
1,960 Å absorption	$^1S_0 \longrightarrow {}^1P_1$
2,470 Å emission	$^1P_1 \longrightarrow {}^1S_0$

In contrast to the earlier model, the configurational coordinate curves for the triplet and singlet emitting states are very similar.

This 2,470-Å emission was not previously observed, because it falls within the 2,500-Å absorption band, and thus the emitted light is strongly reabsorbed. The visible blue emission remains for the present unexplained. Johnson and Williams suggest that it originates also from isolated Tl^+ ions, but in a different excited or vibrational state.

Other emission bands appear at high thallium concentrations, arising from Tl^+ pairs and other imperfections, such as molecular complexes of the form $Tl(Cl_n)$ (P. Pringsheim, Ewles and Joshi).

KCl and TlCl may be mixed in all proportions. Sunit Chandra Sen has shown that in such mixtures two phases exist:

(*a*) KCl activated by a large amount of thallium, in which one recognizes the emission bands described by the above authors;

(*b*) TlCl contaminated by potassium. TlCl seems to be luminescent in the pure state, the luminescence being due to structural defects (Sokolov and Tolstoi). Potassium acts here as a quencher of this luminescence.

The 3,050-Å luminescence emission from isolated Tl^+ centres in KCl is not polarized, except at temperatures near that of liquid helium (Klick and Dale Compton). This polarization is obtained when the exciting radiation is itself polarized. Theoretically, the spatial degeneracy of the centre may be removed when it is placed in the crystal lattice (Jahn–Teller effect), but the energy difference between these sub-levels is surely extremely small. However, at liquid helium temperature a preferential orientation of the centre may appear. The observed polarization is for centres distorted along the (100) directions. On the other hand, the blue emission is not polarized, even at liquid helium temperature.

The emission from centres whose structure is fundamentally asymmetric, such as Tl^+-pairs, probably shows much more pronounced polarization effects.

III. CALCULATION OF THE EMISSION AND ABSORPTION SPECTRA FROM THE CONFIGURATIONAL COORDINATE MODEL

1. Statement of the problem

We have seen how we can obtain from the configurational coordinate model the positions of the maxima of the absorption and emission curves using the Franck–Condon principle. We now consider the form and magnitude of these bands.

For the oscillators $\mathscr{U}^g$ and $\mathscr{U}^e$ we have equi-distant vibrational levels which we denote by the symbol m in the ground state and n in the excited state. In KCl(Tl) and with the presentation due to Williams these arise from vibrational levels of the Cl^- ions (coupled to the rest of the lattice) surrounding the Tl^+ activator ion.

For the transition from the vibrational level n of the excited state to the level m of the ground state there is an emission of a line of frequency $h\nu_{nm}$

$$h\nu_{nm} = E_n^e - E_m^g$$

The assembly of these 'lines' for all possible values of n and m forms the emission band. The same ideas apply to the absorption.

In practice, the bands cannot be resolved into lines since the lines ν_{nm} are broadened by other vibrational modes of the lattice which are not taken account of in the diagram having a single configurational coordinate. However, in one sample of $Zn_2SiO_4(Mn)$, C. Vlam has found a resolution of the emission spectrum into 19 lines when the temperature is lowered to 15°K.

There is a non-zero band width at absolute zero: the emission transition begins from $n = 0$, but because of the zero point energy of vibration can be to various of the m levels. The explanation of the residual large width (one or more tenths of an electron volt) of these bands at absolute zero is one of the successes of this model. The idea of introducing the zero-point energy in consideration of luminescence characteristics was due to M. Schön. If the temperature is sufficiently high, then the band width increases because the emission transition can occur from levels with $n \neq 0$. Experiment indicates that the form of

the absorption and emission bands, $\sigma(h\nu)$ and $I(h\nu)$ respectively, is in general sensibly gaussian. We first define the notation used:

The parameters of a gaussian distribution: If $I(h\nu)$ is a gaussian dis-
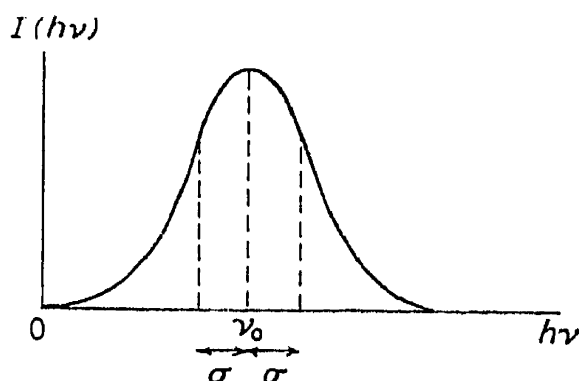
Fig. II.7 *The Gaussian distribution*

tribution about a mean value $h\nu_0$, the normalized distribution is given by

$$I(h\nu) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(h\nu-h\nu_0)^2}{2\sigma^2}\right]$$

with

$$\int I(h\nu)d(h\nu) = 1$$

and

$$\overline{h\nu} = h\nu_0 = \int I(h\nu)h\nu d(h\nu)$$

The mean square deviation is

$$\Delta(h\nu) = \sqrt{\int (h\nu-h\nu_0)^2 I(h\nu)d(h\nu)} = \sigma$$

The curve $I(h\nu)$ is symmetrical about the mean energy $h\nu_0$ and has points of inflexion for $h\nu = h\nu_0 \pm \sigma$. The width at half maximum is $2L$ where

$$L^2 = 2\sigma^2 \log_e 2$$

2. Calculation of energy distribution in the spectrum

This can be made as for diatomic molecules. We set out the expression for the light intensity for the dipole case which is

$$I(h\nu_{nm}) = \frac{64\pi^4\nu_{nm}^4}{3c^3} |\mu_{nm}|^2$$

and we assume that μ_{nm} is proportional to the overlap integral (Condon approximation).

If x are the electron coordinates, r the configurational coordinate of the ions, then we separate the electronic wave function $\phi(\mathrm{x})$ and the vibrational wave function $\psi(r)$ and thus postulate

$$\mu_{nm} = \int \phi_e{}^*(\mathrm{x})\psi_n{}^{*e}(r - r_0)ex\phi_g(\mathrm{x})\psi_m{}^g(r) \ \mathrm{dx} \ \mathrm{d}r$$

The factor

$$\mu_{eg} = \int \phi_e{}^*(\mathrm{x})ex\phi_g(\mathrm{x}) \ \mathrm{dx}$$

depends only on the electronic states e and g, and so we have

$$\mu_{nm} = \mu_{eg} \int \psi_n{}^{*e}(r - r_0)\psi_m{}^g(r) \ \mathrm{d}r$$

To simplify matters we change the notation by reference to paragraph II above; the origin of the configurational coordinate curve
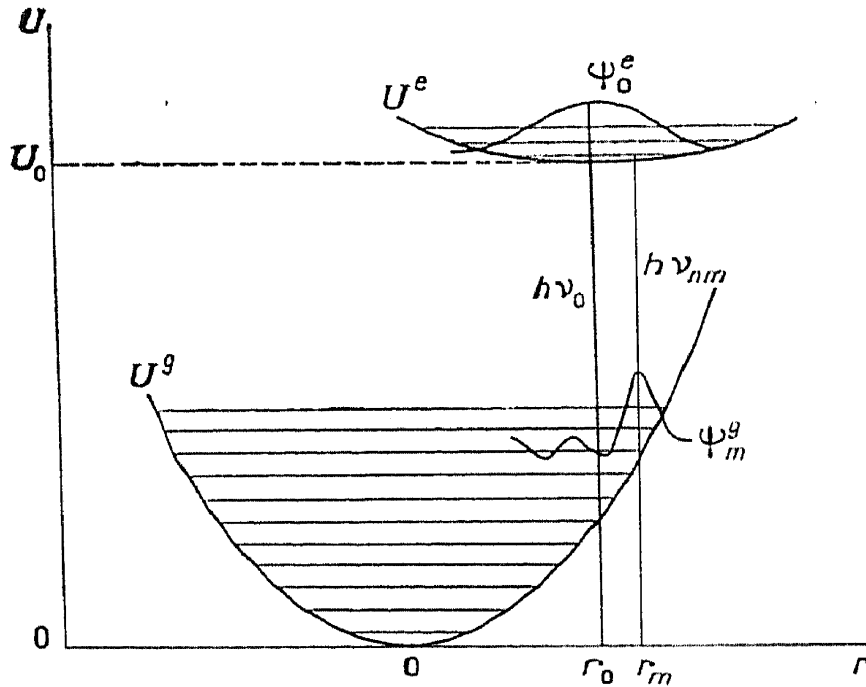
Fig. II.8 *Calculation of emission spectra:*
ν_0 *is the frequency at the band maximum;*
ν_{nm} *is one of the possible emission frequencies*

corresponds to the minimum in $\mathscr{U}^g$ and r_0 is the displacement of the excited state minimum of $\mathscr{U}^e$ relative to the ground state minimum $\mathscr{U}^g$:

$$\mathscr{U}^g(r) = \tfrac{1}{2}k_g r^2; \qquad \mathscr{U}^e(r) = \tfrac{1}{2}k_e(r - r_0)^2 + \mathscr{U}_0$$

The functions $\psi_m{}^g(r)$ and $\psi_n{}^e(r-r_0)$ are thus the eigenfunctions of the harmonic oscillator

$$\psi_m{}^g(r) = N_m \exp\left[-\tfrac{1}{2}\left(\frac{r}{a_g}\right)^2\right] H_m\left(\frac{r}{a_g}\right)$$

where H_m is the Hermitian polynomial, N_m a normalization factor, and a_g is the classical amplitude of the zero-point vibration:

$$a_g{}^2 = \frac{\hbar}{\sqrt{k_g M}} = \frac{\hbar}{M\omega_g}$$

$$\nu_g = \frac{1}{2\pi}\sqrt{\frac{k_g}{M}}; \qquad \omega_g = \sqrt{\frac{k_g}{M}}$$

$h\nu_g = \hbar\omega_g$ is the vibrational quantum of the ions in the ground state: analogous notations are used for the excited state.

M is the mass of those ions which are vibrating, i.e. the mass of the six Cl^- ions in KCl(Tl) to a first approximation. To a second degree of approximation Williams gives

$$M = 6M_{Cl}{}^* \quad \text{where} \quad M_{Cl}{}^* = M_{Cl} + \alpha^2 M_K$$

α being a coupling constant equal to 0·43.

3. Calculation using a semi-classical approximation

The quantum number m reached after emission is high (and in the same way the number n reached after absorption); we have seen that it is about 67 for KCl(Tl). Thus $|\psi_m{}^g(r)|^2$ tends towards the classical density distribution which possesses a very sharp maximum around the classical amplitude r_m given by

$$\mathscr{U}^g(r_m) = \tfrac{1}{2}k_g r_m{}^2 = (m+\tfrac{1}{2})h\nu_g$$

In contrast, the initial state of the transition must be treated quantum mechanically.

Case for low temperatures. At low temperatures the emission will begin from the state $n = 0$, the only one occupied in thermal equilibrium:

$$\mu_{nm} \approx \text{const. } \psi_0{}^e(r_m - r_0)$$

Now ψ_0 is a gaussian function and thus so also is μ_{nm}

$$|\psi_0{}^e(r-r_0)|^2 = N_0{}^2 \exp\left[-\left(\frac{r-r_0}{a_e}\right)^2\right]$$

$$|\mu_{0m}|^2 = \text{const. } \exp\left[-\left(\frac{r_m-r_0}{a_e}\right)^2\right]$$

a_e is the vibrational amplitude at the zero-point energy:

$$a_e^2 = \frac{\hbar}{\sqrt{k_e M}} = \frac{\hbar}{M \omega_e}$$

By differentiation of $\mathscr{U}^g(r)$ in the region of $r = r_0$:

$$\mathscr{U}^g(r_m) - \mathscr{U}^g(r_0) = -h(\nu_{0m} - \nu_0) = k_g r_0(r_m - r_0)$$

Thus we obtain

$$\mu_{0m}^2 = \text{const. } \exp\left[-\frac{(h\nu_{0m} - h\nu_0)^2}{k_g^2 r_0^2 a_e^2} \right]$$

The moment σ_e of the emission band is given by the expression

$$2\sigma_e^2 = k_g^2 r_0^2 a_e^2$$

while the moment σ_a of the absorption band is given by

$$2\sigma_a^2 = k_e^2 r_0^2 a_g^2$$

We can alter these formulae to indicate the mean number S_e [$= 67$ in KCl(Tl)] of thermal vibrational quanta emitted after the photon

$$h\nu_0 = \mathscr{U}_0 - S_e h\nu_g$$
$$\tfrac{1}{2} k_g r_0^2 = S_e h\nu_g$$

and so $\sigma_e^2 = S_e(h\nu_g)^3 / h\nu_e$ for the emission band.

In a similar way, if we introduce S_a [$= 41$ for KCl(Tl)], the number
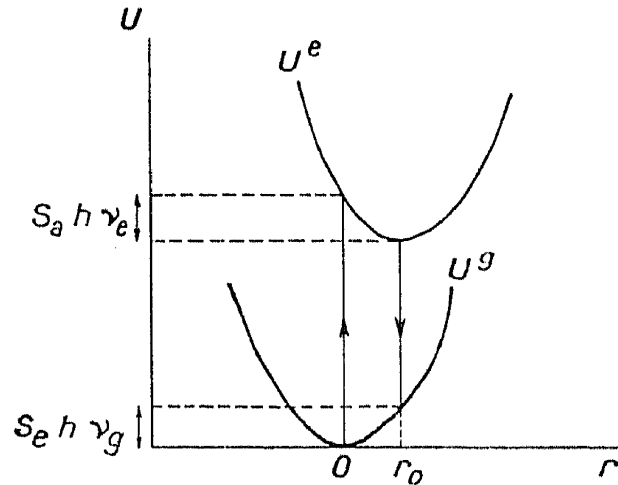
Fig. II.9 *Introduction of the parameters S_e and S_a*

of thermal vibrational quanta emitted after absorption of a photon

$$h\nu_0 = \mathscr{U}_0 + S_a h\nu_e$$
$$\tfrac{1}{2} k_e r_0^2 = S_a h\nu_e$$

and so $\quad\quad\quad\quad \sigma_a^2 = S_a \dfrac{(h\nu_e)^3}{h\nu_g}$

In the case where the vibrational frequencies ν_g and ν_e are equal

$$\sigma_a = \sigma_e = \sigma; \qquad S_a = S_e = S$$

$$\sigma^2 = S(h\nu_{\text{phonons}})^2$$

The widths of the absorption and emission bands are thus the same. However, for KCl(Tl) ν_e and ν_g are quite different: we have already seen that

$$h\nu_g = 0.016 \text{ eV} \quad \text{and} \quad h\nu_e = 0.010 \text{ eV}$$

and so $\dfrac{\sigma_e}{\sigma_a} \approx 3$ to 4 near to absolute zero, which is so experimentally (Johnson, Williams, Studer). This ratio is only about 2 at ordinary temperatures.

Case for any temperatures. The fraction of excited centres to be found in the vibrational state n if thermal equilibrium is attained between absorption and emission† is

$$p_n = \frac{\exp\left(-nh\nu_e/kT\right)}{\displaystyle\sum_{n=0}^{\infty} \exp\left(-nh\nu_e/kT\right)}$$

and so $|\mu_{nm}|^2$ will be affected by the factor p_n and we then have

$$I(h\nu_{nm}) \propto p_n \, | \, \psi_n^{e}(r_m - r_0) \, |^2$$

The emission intensity at frequency ν can be given as a double summation over n and m, remembering that $E_n^e - E_m^g = h\nu$. This means that

$$I(h\nu) \propto \sum_n \sum_m p_n \, | \, \psi_n^{e}(r_m - r_0) \, |^2 \, \delta(E_n^e - E_m^g - h\nu)$$

We now show that the distribution remains gaussian. We use the Franck–Condon principle, that is, we assume that emission occurs without change in the position of the ions‡ and this position corre-

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† Evidence for this rapid 'thermostating' of the excited centres by the crystal lattice is given by the fact that the luminescence quantum yield for KCl(Tl) is independent of the wavelength of the exciting light, as long as it falls into the $^{1}S_0 \longrightarrow {}^{3}P_1$ absorption band of the Tl⁺ ions (Louchtchik, Tech., Louchtchik, N. E. and Shvarts). This is true even if the exciting radiation is situated on the long-wave side of the absorption band, for which (as a result of the overlap between emission and absorption bands) part of the emission results from an anti-Stokes process.

‡ Actually Franck and Condon did not give this principle in such a restricted form. It is the most intense lines which are emitted without change in the position of the ions. We are limited to a consideration of the latter.

sponds to the classical vibrational amplitude r_m as defined above. We can then replace

$$\delta(E_n{}^e - E_m{}^g - h\nu)$$

by

$$\delta(\mathscr{U}^e(r_m) - \mathscr{U}^g(r_m) - h\nu)$$

Furthermore, we can replace the summation over the final vibrational states (m) by an integral:

$$I(h\nu) \propto \int \left[\sum_n p_n \mid \psi_n{}^e(r_m - r_0) \mid^2 \right] \delta\left[\mathscr{U}^e(r_m) - \mathscr{U}^g(r_m) - h\nu \right] \mathrm{d}r_m$$

The summation makes use of the Mehler formula for the Slater summations of the harmonic oscillator:

$$\sum_{n=0}^{n=\infty} \frac{e^{-(n+1)\alpha}}{\sqrt{\pi} 2^n n!} H_n{}^2(x) e^{-x^2} = \frac{1}{(2\pi \sinh \alpha)^{1/2}} \exp\left[-x^2 \tanh\left(\frac{\alpha}{2}\right) \right]$$

where

$$\alpha = h\nu_e / kT$$

We have thus

$$\sum_{n=0}^{\infty} p_n \mid \psi_n{}^e(r_m - r_0) \mid^2 = \frac{e^{\alpha/2}(1 - e^{-\alpha})}{(2\pi \sinh \alpha)^{1/2}} \exp\left[-\left(\frac{r_m - r_0}{a_e}\right)^2 \tanh\left(\frac{\alpha}{2}\right) \right]$$

and

$$I(h\nu) \propto \int \exp\left[-\tfrac{1}{2}k_e(r_m - r_0)^2 \cdot \frac{2}{h\nu_e} \tanh\left(\frac{h\nu_e}{2kT}\right) \right] \\ \times \delta(\mathscr{U}^e(r_m) - \mathscr{U}^g(r_m) - h\nu) \, \mathrm{d}r_m$$

We now take a new variable $x = \mathscr{U}^e(r_m) - \mathscr{U}^g(r_m)$ for the purpose of integration and obtain

$$I(h\nu) \propto \int \exp\left[-\tfrac{1}{2}k_e(r_m - r_0)^2 \cdot \frac{2}{h\nu_e} \cdot \tanh\left(\frac{h\nu_e}{2kT}\right) \right] \delta(x - h\nu) \frac{\mathrm{d}r_m}{\mathrm{d}x} \cdot \mathrm{d}x$$

and since

$$\int f(x)\delta(x - h\nu) \, \mathrm{d}x = f(h\nu)$$

we have finally

$$I(h\nu) \propto \left\{ \exp\left[-\tfrac{1}{2}k_e(r - r_0)^2 \cdot \frac{2}{h\nu_e} \tanh\frac{h\nu_e}{2kT} \right] \frac{\mathrm{d}r}{\mathrm{d}x} \right\}_{x=h\nu}$$

r being related to the emission frequency by the linear relation

$$-h(\nu - \nu_0) = k_g r_0(r - r_0)$$

The exponential factor gives an essentially gaussian form to $I(h\nu)$. At high temperatures

$$I(h\nu) \propto \exp\left[-\tfrac{1}{2}k_e(r - r_0)^2 \cdot \frac{1}{kT} \right] \frac{\mathrm{d}r}{\mathrm{d}x}$$

which is a classical formula, the exponential being that of the Boltzmann distribution, and gives the probability that the emitting system will be in the configuration r allowing by means of the Franck–Condon principle the emission of a photon $h\nu$.

This classical approximation was used by Williams for KCl(Tl) to which it applies well at liquid air temperature (90°K) which is sufficiently large. For KCl(Tl) the quantum $h\nu_e$ is very small (0·010 eV). In contrast for CaWO$_4$(Pb) it reaches 0·05 eV and Vlam has found that the classical approximation is only valid at temperatures well above room temperature.

At $T = 0$ the hyperbolic term $\left(\tanh \dfrac{h\nu_e}{2kT}\right)$ is equal to unity and we obtain the expression first derived for low temperatures. Finally the band width L varies with temperature according to the relation

$$L_e(T) = L_e(0)\left[\tanh \frac{h\nu_e}{2kT}\right]^{-1/2}$$

A typical example of this variation is given in Fig. II.10. The theoretical curve has a point of inflexion and the width $L(T)$ finally
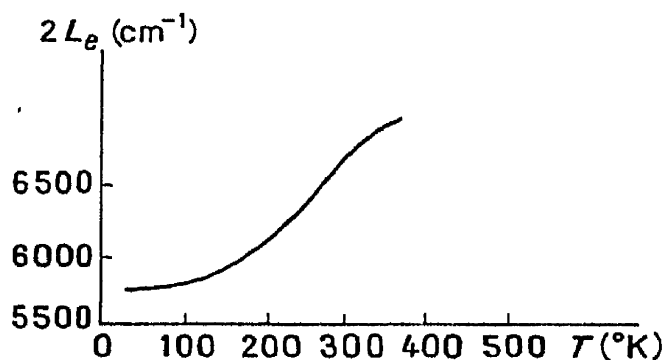
Fig. II.10 *Variation of luminescence emission band width (at half-band height) with temperature for a CaWO$_4$(Pb) phosphor*
(After Vlam)

varies as $\sqrt{T}$ (classical approximation). However, in the figure this temperature region is not reached.

For the width of the absorption band $h\nu_e$ is replaced by $h\nu_g$ in the above formulae:

$$L_a(T) = L_a(0)\left[\tanh \frac{h\nu_g}{2kT}\right]^{-1/2}$$

The introduction of the factor 'tanh' may be understood in the following manner: in the expression for the moment of the emission

band, for instance, established above for the case of emission at $0°K$:

$$2\sigma_e^2 = k_g^2 r_0^2 a_e^2$$

the amplitude of vibration of the ions at the zero-point energy a_e must now be replaced by the mean square value $\overline{a_e(n)}$ of all the amplitudes in the different vibrational states n. These amplitudes are defined by

$$\tfrac{1}{2}k_e a_e^2 = (0+\tfrac{1}{2})h\nu_e$$

$$\tfrac{1}{2}k_e a_e(n)^2 = (n+\tfrac{1}{2})h\nu_e$$

$$a_e \longrightarrow \overline{a_e(n)} = \sqrt{\Sigma p_n a_e(n)^2}$$

This summation is straightforward and leads to

$$\overline{a_e(n)} = a_e . \left[\tanh \frac{h\nu_e}{2kT} \right]^{-1/2}$$

The case where the configurational space is many-dimensional. In the general case, we have seen (page 39) that several coordinates must be used in order to describe the configuration of the ions interacting with the luminescence centre. We shall assume that the potential energies have been put into the diagonal form:

$$\mathscr{U}^g(r_1, r_2 \ldots) = U_0^g + \Sigma_i \tfrac{1}{2}k_{gi}(r_i - r_{i0}^g)^2$$

$$\mathscr{U}^e(r_1, r_2 \ldots) = U_0^e + \Sigma_i \tfrac{1}{2}k_{ei}(r_i - r_{i0}^e)^2$$

This is indeed the case in Williams's calculation, with 2 coordinates, r_1 describing the position of the Cl^- ions neighbouring the Tl^+ activator ion, and r_2 describing the position of the next nearest neighbours, i.e. K^+ ions.

The position of the maximum of the emission band is then given by

$$h\nu_0 = \mathscr{U}_0^e - \mathscr{U}_0^g - \Sigma\tfrac{1}{2}k_{gi}(r_{i0}^e - r_{i0}^g)^2$$

and the corresponding moment by

$$2\sigma_e^2 = \sum \frac{k_{gi}(r_{i0}^e - r_{i0}^g)a_i^{e\,2}}{\tanh (h\nu_i^e/2kT)}$$

It is seen that, theoretically, this result cannot be obtained by means of a one-dimensional configuration diagram, except when all the frequencies ν_i^e are equal. However, for KCl(Tl) the difference between the results obtained in this way and the results obtained by Williams and co-workers in eliminating the second configurational coordinate r_2 is almost insignificant (about 0·15 eV in the position of the band).

The general case, where $\mathscr{U}^e$ and $\mathscr{U}^g$ are in a non-diagonal tensor form, has been treated by Kubo and Toyozawa, and by K. Maeda (1959).

4. Quantum-mechanical calculation for the case where the ion vibrations υ_e and υ_g are equal

We put $h\nu_e = h\nu_g = \hbar\omega$ as the vibrational quantum for the ions and ν the frequency of the emitted photon. We can now give a rigorous calculation of the overlap integral

$$J(h\nu_{nm}) = \int \psi_n^{*e}(r-r_0)\psi_m^{g}(r) \, dr$$

which occurs in the matrix element μ_{nm} (J. Ruamps).†

We have seen that this assumption is not valid for KCl(Tl) ($h\nu_e = 0.01$ eV; $h\nu_g = 0.016$ eV), but it is all right for F centres in the same KCl crystal where from Klick we have

$$h\nu_e \approx h\nu_g \approx 0.011 \text{ eV}$$

We have thus a single parameter S which is the mean number of thermal vibrational quanta emitted after the optical transition resulting in absorption or emission of a photon. S is given by

$$\tfrac{1}{2}kr_0^2 = S\hbar\omega$$

In emission the line is of about a frequency ν_0 given by

$$h\nu_0 = U_0 - S\hbar\omega$$

and in absorption

$$h\nu_0 = U_0 + S\hbar\omega$$

The Stokes shift between absorption and emission is thus $2S\hbar\omega$. U_0 is always the electronic energy difference between the ground and excited states. Consider the emission, for example. An emission of frequency ν_{nm} occurs by transition from a vibrational state n to a vibrational state m, the transition being followed by emission of $p = m-n$ vibrational quanta (mean value of $p = S$):

$$h\nu_{nm} = U_0 + (n+\tfrac{1}{2})\hbar\omega - (m+\tfrac{1}{2})\hbar\omega = U_0 - p\hbar\omega$$

The overlap integral $J(h\nu_{nm})$ is given by a formula due to Erdelyi

$$J(h\nu_{nm}) = \Lambda_n^p(S); \qquad (p = m-n)$$

$\Lambda_n^p(S)$ being a normal Laguerre function:

$$\Lambda_n^p(S) = \left[\frac{n! e^{-S} . S^p}{(n+p)!}\right] L_n^p(S)$$

† In a recent publication (1960), J. Ruamps has described an extension of this method for the case $h\nu_e \neq h\nu_g$. The form of the emission band $I(h\nu)$ cannot be explicitly derived, but the expressions of the first and second moments are given as developments in series.

In addition, let us remark that the anharmonicity effects are probably less important for the case of luminescence centres in a solid than for the spectra of diatomic molecules. However, precise computations must take these effects into account. See the paper by Rebane and Sild, quoted in the bibliography.

C

where

$$L_n{}^p(S) = \frac{1}{n!} \cdot e^S S^{-p} \left(\frac{d}{dS}\right)^n (e^{-S} \cdot S^{n+p})$$

However, the mean frequency ν can be emitted by transition from any n level: ν only depends on p. Thus we have

$$I(h\nu) \propto \sum_{\substack{n=0 \\ p=\text{const.}}}^{n=\infty} [A_n{}^p(S)]^2 \frac{e^{-n\alpha}}{\sum_0^\infty e^{-n\alpha}}$$

α is, as previously, given by $\hbar\omega/kT$.

This summation is made by using the Myller–Lebedeff formula:

$$I(h\nu) \propto e^{p\alpha/2} e^{-S \coth (\alpha/2)} I_p\left(\frac{S}{\sinh (\alpha/2)}\right)$$

If $\bar{n} = 1/(e^\alpha - 1)$, the mean number of vibrational quanta excited at temperature T, we can then write

$$I(h\nu) \propto \left(\frac{\bar{n}+1}{\bar{n}}\right)^{p/2} e^{-S(\bar{n}+1)} I_p[2S\sqrt{\bar{n}(\bar{n}+1)}]$$

where $I_p(x)$ is the Bessel function with complex argument $i^{-p} J_p(ix)$, i.e.

$$I_p[2S\sqrt{\bar{n}(\bar{n}+1)}] = \sum_{s=0}^\infty \left[\frac{S\sqrt{\bar{n}(\bar{n}+1)}}{s!(s+p)!}\right]^{2s+p}$$

This formula is due to Huang and Rhys, Pekar, Lax, Meyer, O'Rourke, &c. We have obtained it by using the configurational co-ordinate model, but it is usually derived by using the model where the interaction between centre and lattice is obtained by representing the latter by its assembly of phonons (cf. para. II.3); $\hbar\omega$ is then the photon energy in the perfect lattice instead of the vibrational quantum for the ionic neighbours of the centre. Apart from this detail the formulae obtained are identical.

According to Klick the configurational coordinate model is the better one for F centres: we have seen that the common value of $\hbar\omega_e$ and $\hbar\omega_g$ which gives the best interpretation of the observed spectra is 0·011 eV, which for the optical branch of the perfect lattice vibrations of KCl (optical phonons) is 0·028 eV.

We shall not give the calculations for the model of Huang and Rhys and Pekar, but simply indicate that each term in the summation for I_p appears as a contribution to $I(h\nu)$ from the transitions in which

s oscillators lose a quantum and $s+p$ gain a quantum and the total transition is effected by an emission of p phonons.

We can verify that the mean value of p is indeed equal to S; the mean value of p^2 is, according to Lax

$$\overline{p^2} = S(2\bar{n}+1) = S \coth \left(\frac{\hbar\omega}{2kT} \right)$$

such that the moment σ^2 of $I(h\nu)$ has the value

$$\sigma^2 = \int (h\nu - h\nu_0)^2 I(h\nu)\, \mathrm{d}(h\nu) = S(\hbar\omega)^2 \left[\tanh \left(\frac{\hbar\omega}{2kT} \right) \right]^{-1}$$

which agrees with the expressions obtained by the semi-classical approach for this moment at absolute zero and for its variation with temperature.

When $x = 2S\sqrt{\bar{n}(\bar{n}+1)}$ is large compared with unit ($\bar{n}$ or S large) we have the asymptotic form

$$I_p(x) \longrightarrow \frac{e^x}{\sqrt{2\pi x}}\, e^{-p^2/2x}$$

$I(h\nu)$ is thus a gaussian function centred on $p = S$. Not only the moment σ^2 but the form of the emission band are identical to those obtained in the semi-classical approximation. This expression for I_p is already accurate to 5 per cent if $x = 4$.

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Experimental Determination and Use of Configurational Coordinate Diagrams

1. Tungstates, willemites, halophosphates, &c.

As discussed in the previous chapter, F. E. Williams was able for the case of the transition $^1S_0 \leftrightarrow {}^3P_1$ in KCl(Tl) to obtain the energy versus configurational coordinate curves for ground and excited states and from them to obtain absorption and emission spectra which could be compared with experiment. This is a rather exceptional case. However, it is possible to obtain from experimental results a configurational coordinate diagram and to confirm this with other results. Such diagrams have been used for the alkali halides, willemites, tungstates, halophosphates (Fonda), calcium oxide (Janin and Crozet), all being cases of phosphors in which luminescence is not very closely associated with photoconductivity. They have also been applied to doubly activated phosphors such as $Ca_3(PO_4)_2$(Ce–Mn), &c., to explain the process of sensitization (Botden).

In the case of photoconducting phosphors of the ZnS(Cu) type the use of configurational coordinate diagrams has been somewhat criticized, especially by F. Seitz. They certainly cannot be applied to the kinetic processes which occur after absorptions and before final emission. However, they can be applied to processes which are confined to the emission centres. The optical and thermal activation of electrons from traps may also be described with a configuration diagram (see Chapter VII), but, as a general rule in these phosphors, not on the *same* diagram as for the luminescence centres.

We shall consider some examples briefly:

(A) *Tungstates.* These are sometimes used in X-ray fluorescent screens. The configurational coordinate diagram was derived by Vlam. The typical experimental data are as follows: for a $CaWO_4$(Pb) phosphor containing 1 per cent by weight of lead.

TABLE III.1

Emission spectra of $CaWO_4(Pb)$†

Temp. °K	$h\nu_0$ (eV)	$2L_e$ (eV)
20	2·68 (4,630 Å)	0·71
90	2·69 (4,620 Å)	0·725
288	2·73 (4,540 Å)	0·82
410	2·77 (4,480 Å)	0·87

We see that the width of the emission does not change significantly with temperature (1/5 increase between 90°K and 140°C). From the relation

$$L_e(T) = L_e(0)[\tanh h\nu_e/2kT]^{-1/2}$$

therefore, we find a high value for the vibrational quantum energy in the excited state of

$$h\nu_e = 0\cdot050 \text{ eV}$$

and in the ground state

$$h\nu_g = 0\cdot10 \text{ eV}$$

the distance between the equilibrium position of the ions in the excited and ground states r_0 is estimated to be

$$r_0 = 0\cdot20 \text{ Å}$$

We assume that the atomic group responsible for the emission is the tungstate ion WO_4^{2-}. Vlam identifies the configurational coordinate r with the distance of the tungsten from the four surrounding oxygen ions.

(B) *Willemite:* $Zn_2SiO_4(Mn)$. Manganese functions as an activator in a large number of fluorescent solids. The emission spectra of $Zn_2SiO_4(Mn)$ have been studied by Kröger, Szigeti and Nagy and by Vlam, &c. The configurational coordinate diagram was derived by Klick and Schulman.

TABLE III.2

Emission spectra of $Zn_2SiO_4(Mn)$

T. °K	$h\nu_0$ (eV)	$2L_e$ (eV)
20	2·40	0·11
90	2·39 (5,200 Å)	0·13
288	2·38	0·19
410	2·37 (5,220 Å)	0·23

The band width doubles between about 180°C and 140°C and the

† The notation of the previous chapter is used.

vibrational quantum is much smaller than for $CaWO_4(Pb)$ phosphors. Klick and Schulman give

$$hv_e = 0.025 \text{ eV}$$
$$hv_g = 0.04 \text{ eV}$$
$$r_0 = 0.06 \text{ Å}$$

The value of r_0 is particularly small, and as a result the approximation made in differentiating $U^g(r)$ in the region of $r = r_0$ to obtain a linear relation between the emission hv and r is not satisfactory. The form of the emission spectral curve is clearly different from
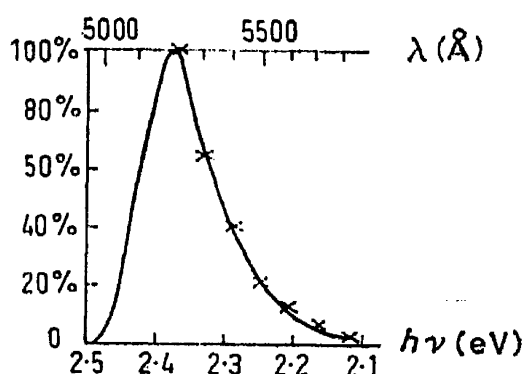
Fig. III.1 *Low temperature (20°K) emission spectrum o,*
$Zn_2SiO_4(Mn)$

Continuous curve: observed spectrum (C. Vlam)
Cross points: computed spectrum (Klick and Schulman)

gaussian (in the quantum theory of II.4 this corresponds with the case where the parameter S is small and the asymptotical approximation to the gaussian form of I_p can no longer be used). The observed spectrum is asymmetric, showing a 'tail' on the longer wavelength side extending into the red. Before the work of Klick and Schulman, attempts were made to resolve the spectrum into a number of gaussian components without trying to attribute them to different well-defined centres.

The emission transition is attributed to a spin reversal of one of the $3d$ shell electrons of the Mn^{2+} ion. The mode of vibration is a radial one for the four oxygen ions surrounding the manganese.

(C) If we apply the configurational coordinate model to ZnS(Cu) phosphors the band width increases with temperature in an intermediate manner relative to $CaWO_4(Pb)$ and $Zn_2SiO_4(Mn)$ phosphors

the vibrational quantum being between 0·03 and 0·04 eV.† It might be associated with vibrations of the sulphur ions surrounding the copper ions.

(*D*) *Halophosphates*. Among phosphors used in fluorescent lamps the halophosphates have first place as they enable a wide range of colours to be achieved by variations in their compositions. From a theoretical aspect they demonstrate the effect of activator environment on emission spectrum. The formula of the halophosphates is

$$3Ca_3(PO_4)_2, Ca \left| \begin{matrix} F_2 \\ Cl_2 \end{matrix} \right. (Mn^{2+}Sb^{3+})$$

They can be excited by 2,537-Å radiation or by cathode rays. Antimony gives two emission bands as follows (the most intense one is underscored)

$$\underline{4,870\ Å} \quad \text{and} \quad 3,960\ Å$$

Some theoretical light on the behaviour of this activator has recently been thrown by F. E. Williams (1960). It occurs in the form Sb^{3+} (Butler and Jerome), which is isoelectronic with In^+ and so its scheme of energy levels is very similar to Tl^+, except for a smaller spin-orbit coupling. Except at compositions (near to the pure chlorophosphate) where structural changes are expected, the position of the antimony peak shows a negligible dependence on the ratio Cl_2/F_2 since the nearest neighbours of the Sb^{3+} in the lattice are six O^{2-} ions. However, the intensity of the peak suffers a noticeable change with this ratio.

The manganese is present in the divalent state Mn^{2+}. Its emission spectrum is conveniently described by two gaussian bands,‡ which are progressively displaced as the chlorine is replaced by fluorine from

$$\underline{5,950\ Å} \quad \text{and} \quad 6,550\ Å$$
$$\text{to} \quad \underline{5,700\ Å} \quad \text{and} \quad 6,250\ Å$$

The vibrational quantum $h\nu_e$ for the main emission band of Mn^{2+} is about 0·035 eV (Vlam). Comparison with the value of 0·025 eV for willemite shows that the value depends on both the activator and its surroundings.

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† The quantum energy and also the band width of the emission vary markedly with the method of preparation of the specimen: see H. PAYEN DE LA GARANDERIE and D. CURIE, *Comptes Rendus*, **248** (1959), p. 3151.

‡ This is really only an empirical way of describing a single asymmetric band.

The life time of the transition giving emission from the Sb^{3+} ions is about 1/1500 sec, while that for the Mn^{2+} emission is about 1/75 sec. The antimony is necessary as a sensitizer for excitation of the manganese emission (see Fonda, *Brit. J. Applied Physics, suppl.* **4**, 1955). As sole activator it gives a light-blue emission. With similar concentrations of antimony and manganese ($\approx$ 2 per cent) daylight simulation can be obtained. Increasing the manganese content gives warmer tones, but truly red phosphors are not obtained; the efficiency of the 'warm white' lamps made using these phosphors can reach 60–70 lumens per watt (Vanmaker and Ouweltjes).

2. Relation between F centre absorption bands and the luminescence emission ascribed to F centres

The colour centres of F type form the most investigated lattice defects in the alkali halides. They are defined as halogen ion vacancies which have captured an electron. For other types of defects or imperfections in these crystals reference may be made, for example, to C. Kittel (*Introduction to Solid State Physics*, J. Wiley (1956), pp. 491–502).

F centres can be produced by a stoichiometric excess of the cations. For example, a sodium or potassium chloride crystal can be heated in sodium or potassium vapour at a temperature of about 100°C below the melting-point and then cooled quickly so that colloidal aggregation of the excess ions (or vacancies) does not occur. The observed crystal colours due to the presence of F centres are as follows:

NaCl	Yellow
KCl	Magenta
KBr	Blue
KI	Blue-green

Since the whole crystal must be electrostatically neutral the excess of positive ions must be compensated by an equivalent number of electrons captured in the negative ion vacancies forming F centres.

The coloration can be produced by electrolysis in an electric field of a few hundreds of volts per centimetre at a temperature of 100°C or so below the melting-point and also by bombardment with X-rays or high-energy particles which remove electrons from lattice ions which are then captured in the negative ion vacancies; at present such irradiation is the method most often used to colour these

crystals. However, it gives rise to other kinds of centres, e.g. V centres, and the observed effects are much more complex than those produced by additive coloration.

The F-centre absorption is assumed to be due to the transition from the ground state U^g to an excited state U^e, the ground state, being of $1s$ character and the excited state like a $2p$ state (allowed transition). The work of Gudden and Pohl showed that such absorption produces photoconduction at temperatures above 90°K, but this

Conduction band

$2p$ —— $\simeq 0.1$ eV

1.67 eV

$1s$
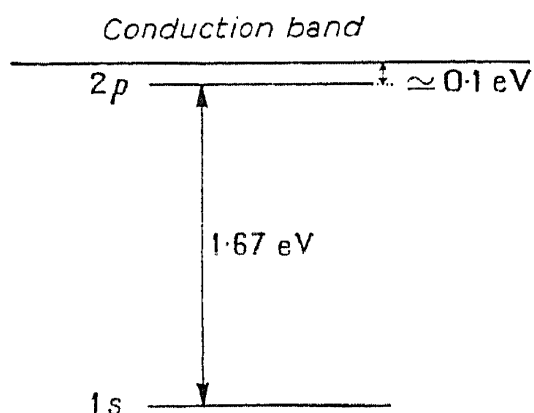
Fig. III.2 *Energy-level scheme for F centres in KBr*

decreases rapidly at lower temperatures. This behaviour is explained by assuming that an activation energy ≈ 0.1 eV is necessary to raise an electron from the excited state U^g into the conduction band (Fig. III.2).

At temperatures not much above 90°K a luminescence emission is observed for the $2p \longrightarrow 1s$ transition. For a long time this F-centre luminescence has been looked for, and it now seems to have been observed during recent years (Botden, van Doorn and Haven), first of all with a very low quantum efficiency ~ 1 to 3 per cent, but more recently with an efficiency of 91 per cent. This is due to the fewer 'killer' centres in the crystals now used. Measurements were made at 77°K, 20°K and 4°K, and the bands were found to change very little in position with temperature. However, a considerable Stokes shift is observed between absorption and emission which makes it difficult to be certain that it is F-centre emission.

A blue-green emission is observed from many alkali-halide crystals when excited by ultra-violet light, but it can be shown that 'pure crystals' are mostly contaminated with oxygen (Maenhout and van der Dorst; Halperin and Lewis): these oxygen ions accompanied by anion vacancies are often responsible for this visible emission. Klick has shown that a detectable green luminescence is produced in NaCl by incorporation of $4 \cdot 10^{-5}$ of copper. In addition, in coloured crystals, a visible and ultra-violet emission may occur when electrons coming from F centres recombine with V-type centres or with the above oxygen impurity centres: such an emission is produced by irradiation in the F band, or during the glow-curve experiment when

the F centres are thermally emptied, but it is not thought to be F-centre luminescence (Bonfiglioli, Brovetto and Cortese; Halperin and Kristianpoller). Phenomena of this kind had been earlier described by G. Perny.

Pekar and Klick have predicted the wavelength region where the emission of F centres would be expected.

The configurational coordinate curves can be drawn without reference to the nature of the coordinate; it is thought to be the distance from the centre of the vacancy to each of the six surrounding K^+ ions. There are four parameters to be determined: the coordinates $\mathcal{U}_0$ and r_0 of the minimum of the excited state curve, the minimum of the curve for $\mathcal{U}^g$ being taken as the origin, and also the coefficients k_e and k_g:

$$\mathcal{U}_g = \tfrac{1}{2}k_g r^2$$
$$\mathcal{U}_e = \tfrac{1}{2}k_e(r-r_0)^2 + \mathcal{U}_0$$

The coefficients k_e and k_g can be replaced by expressions for $h\nu_e$ and $h\nu_g$. As shown by Klick's experiment, a good fit is obtained by assuming $h\nu_e \approx h\nu_g$.

We take now

(i) the position of the F absorption band; Klick used that for extrapolation to absolute zero.

(ii) the relation giving the variation of the band width with temperature

$$L_a(T) = L_a(0)\left[\tanh\frac{h\nu_g}{2kT}\right]^{-1/2}$$

Since this is for the absorption, it gives the vibrational quantum for the ground state $h\nu_g$

$$h\nu_g = 0\cdot011 \text{ eV}$$

and from the band width at 0°K

$$L_a(0) = \sigma_a\sqrt{2\log_e 2}, \qquad \sigma_a^2 = S_a\frac{(h\nu_e)^3}{h\nu_g}$$

and finally the approximate number of phonons S_a emitted after the transition. Klick assumed for KBr the value $S_a = 22$ as given by Huang and Rhys. These data for the absorption enable the configurational coordinate curve to be drawn (see Fig. III.3). From this diagram the position of the emission bands can be deduced. All these bands are in the near infra-red region. Klick used this model but Pekar used that where the crystal is considered in terms of its optical phonons. However, their conclusions are very similar.

TABLE III.3

*Data on absorption and luminescence of
F centres in alkali halides*

| | Absorption maximum | | Emission maximum | |
Crystal	290°K	78°K	calc. obs.	(78°K)
KCl	0·56 μ	0·54 μ	1·1 μ (Meyer)	1·00 μ
KBr	0·63 μ	0·60 μ	1·2 μ (Klick)	1·32 μ
NaCl	0·46 μ	0·45 μ	1·25 μ (Pekar)	1·20 μ

The agreement between theoretical and experimental values seems to show that the observed emission is that from F centres. The vibrational quantum $h\nu_e \approx h\nu_g = 0{\cdot}011$ eV† is clearly smaller than the optical phonon energy $\hbar\omega = 0{\cdot}028$ eV, but the K^+ ions around the vacancy have less binding energy than those in the perfect lattice.

Fig. III.3 *Configurational co-ordinate curves obtained by Klick for F centres in KBr*

The sign of the shift r_0 between the ground and excited equilibrium positions of the ions. The absorption and emission spectra depend on r_0 but not on its sign. We have seen that for KCl(Tl) r_0 appears to be negative, the interionic distance being smaller in the excited state. The reverse seems to be true of F centres. The F-centre electron has a stronger attraction for the K^+ or Na^+ ions in the ground state when its presence in the vacancy is much more localized. This conclusion rests on some work by I. Jacobs, who showed that at high pressures (several thousand atmospheres) the absorption band is moved to higher energies. The effect is attributed to a decrease in the size of the vacancy as the pressure is raised.

M-centre and R-centre luminescence. M-centre emission peaks have also been reported in the infra-red region. In contrast to F-centre emission, the luminescence from M centres is observed at room temperature as well as at liquid-air temperature. The excited state of the M centre is situated deep below the conduction band.

† These values are for KCl: almost identical values are obtained for KBr, but NaCl (N.B. different cation) $h\nu_e \approx h\nu_g \approx 0{\cdot}018$ eV (Klick and Russell).

TABLE III.4

Absorption and luminescence of M centres
(van Doorn and Haven)

	Absorption peak (78°K)	*Emission peak (78°K)*
KCl	0·81 μ	1·06 μ
NaCl	0·71 μ	1·03 μ

The *M*-centre luminescence may be excited either by an irradiation in the *M* absorption band itself or in the *F* absorption band.

No polarization has been found for the *F*-band emission, even when excited by polarized light. This is in agreement with the cubic symmetry of *F* centres. On the other hand, polarization effects are observed for the *M*-centre emission. Let p be the degree of polarization defined by

$$p = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$

($I_{\parallel}$ intensity of the emitted light with polarization parallel to the polarizer, and $I_{\perp}$ intensity of the emitted light with polarization perpendicular to the polarizer.) For exciting radiation absorbed in the *M* band:

$p = 2/3$ for exciting light polarized along the (011) direction
$p = 1/3$ for exciting light polarized along the (001) direction

(Lambe and Dale Compton).

These results indicate that the *M* centre can be represented as a dipole oriented along the face diagonal. Two models have so far been suggested for these centres. Both are in agreement with the above representation:

(*a*) Seitz's model: an electron trapped at a site consisting of two negative-ion vacancies with an adjacent positive-ion vacancy;

(*b*) van Doorn and Haven's model, consisting of an associated pair of *F* centres.

Experiments made by the above authors are in progress which may decide between these models.†

When the exciting light is absorbed in the *F* band and then re-emitted as *M* luminescence, the degree of polarization is smaller and of the opposite sign.

† The model of van Doorn and Haven seems to be the correct one since no electron spin resonance has been detected for *M* centres (see OHKURA and MURASE, *J. Phys, Soc, Japan*, 16, pp. 2076-7, Oct. 1961).

When the coloration is due to high-energy irradiation over a long time, R centres are produced into the crystal in addition to F and M centres. They also give an infra-red emission (between $1 \cdot 2 \, \mu$ and $1 \cdot 5 \, \mu$), but the results reported by different authors are not in good agreement with each other.

3. The Smakula formula

The Smakula formula is often used to determine the concentration of a given impurity by measuring the absorption intensity due to the impurity or defect. If we have N absorbing atoms per cubic centimetre *in vacuo* the absorption section for the photons integrated over as assembly of identical physical states, i.e. with the same matrix element, is given by

$$\int \sigma(E) \, \mathrm{d}E = \frac{8\pi\nu^3}{3c} \mid \mu_{if} \mid^2$$

In experiments we measure the absorption coefficient $k(E) \, \mathrm{cm}^{-1}$ which is given by

$$\int k(E) \, \mathrm{d}E = N \frac{8\pi\nu^3}{3c} \mid \mu_{if} \mid^2$$

We introduce the oscillator strength f_{if}

$$f_{if} = \frac{8\pi^2 m\nu}{3h} \mid r_{if} \mid^2$$

($\Sigma f = 1$ for a harmonic oscillator) and obtain

$$\int k(E) \, \mathrm{d}E = N \frac{\pi e^2 h}{mc} f_{if}$$

For atoms in a medium of refractive index n, c must be replaced by c/n. We must also introduce the ratio effective field E_{eff} to the applied field (due to the electromagnetic radiation): this ratio occurs as a squared term since the dipole moment μ is proportional to the field, but μ^2 appears in the expression for the absorption coefficient.

We can thus write

$$\int k(E) \, \mathrm{d}E = N \frac{\pi n e^2 h}{Kmc} \left[\frac{E_{\mathrm{eff}}}{E} \right]^2 f_{if}$$

Finally we must divide by the dielectric constant K. We then return to the definition of the effective cross-section for absorption:

$$\sigma = \frac{\text{No. of transitions per atom}}{\text{No. of incident photons per cm}^2}$$

The electromagnetic energy density being $KE^2/4\pi$, the number of

photons in the field is K times greater in a medium of dielectric constant K. All these corrections are unimportant as far as the spectral distribution of the radiation is concerned, but they affect its intensity. Since the applied field frequency is large we may assume

$$K = n^2 = 1 + 4\pi\alpha$$

where α is the electronic polarizability of the atoms, and so

$$\frac{E_{\text{eff}}}{E} = 1 + \frac{4}{3}\alpha = \frac{n^2+2}{3}$$

and we obtain

$$\int k(E)\,\mathrm{d}E = N \cdot \frac{1}{n}\frac{\pi e^2 h}{mc}\left(\frac{n^2+2}{3}\right)^2 f_{if}$$

Numerically

$$N_{(\text{cm}^{-3})} = 0 \cdot 821 \cdot 10^{17}\frac{n}{(n^2+2)^2}\frac{1}{f_{if}}\int k(E)\,\mathrm{d}E$$

where k is in cm^{-1} and E is in electron volts. This is the Smakula formula as generalized by Dexter. Dexter observes that the Lorentz–Lorenz expression used for the effective field is valid for a highly localized centre, but for an extensive centre the effective field is close to the value E.† The numerical Smakula formula applies to the case of a line of natural width:

$$k(E) = k_{\max}\frac{\gamma^2/4}{(h\nu - h\nu_0)^2 + \frac{1}{4}\gamma^2}$$

$$\int k(E)\,\mathrm{d}E = \frac{1}{2}\pi k_{\max}\gamma$$

$$N_{(\text{cm}^{-3})} = 1 \cdot 29 \cdot 10^{17}\frac{n}{(n^2+2)^2}\frac{1}{f_{if}}k_{\max(\text{cm}^{-1})}\gamma \text{ (eV)}$$

However, if the band is of gaussian shape, as is more often the case (Dexter), then

$$k(E) = k_{\max}\exp\left[-\frac{(h\nu - h\nu_0)^2}{2\sigma^2}\right]$$

the half-width being $\gamma = 2L = 2\sigma\sqrt{2\log_e 2}$

$$\int k(E)\,\mathrm{d}E = \sigma\sqrt{2\pi}k_{\max} = \frac{1}{2}\sqrt{\frac{\pi}{\log_e 2}}k_{\max}\gamma$$

and we obtain the Smakula formula as corrected by Dexter:

$$N_{(\text{cm}^{-3})} = 0 \cdot 87 \cdot 10^{17}\frac{n}{(n^2+2)^2}\frac{1}{f_{if}}k_{\max(\text{cm}^{-1})}\gamma \text{ (eV)}$$

† K. R. Silbsee proposed the use of the Onsager formula $E_{\text{eff}}/E = \dfrac{3n^2}{2n^2+1}$. This is perhaps not much better than the Lorentz–Lorenz formula, but shows the degree of precision which can be obtained in the theory.

In practice it is necessary, in order to use this formula, to know the oscillator strength by using a specimen with a known impurity concentration. Under these conditions it is not of any interest to use a formula with an exact numerical coefficient.

However, it is now becoming possible to calculate oscillator strengths on a theoretical basis. For comparison with experiment the corrected formula must be used. Experimental values obtained by use of the Dexter formula are listed below:

For the two absorption bands at 1,960 and 2,500 Å in KCl(Tl):

$$f_{1,960} \approx 1; \qquad f_{2,500} \approx 0 \cdot 1 \qquad \text{for } N = 2 \times 10^{-4} \text{ Tl}^+$$
$$f_{1,960} \approx 0 \cdot 3; \qquad f_{2,500} \approx 0 \cdot 07 \qquad \text{for } N = 10^{-2} \text{ Tl}^+$$

The oscillator strength decreases with increase in Tl^+ concentration while new bands appear in both absorption and emission spectra (P. Pringsheim and Joshi).

For the *F*-centre absorption bands:

$$\text{KCl, KBr, NaCl} f \approx 0 \cdot 5 \text{ to } 0 \cdot 6$$
$$\text{KI and CsI} f \approx 0 \cdot 3$$

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Optical Transitions in a
Photoconducting Crystal

Principal characteristics of photoconducting luminescent solids. Copper activated zinc sulphide, ZnS(Cu), has been the most extensively studied: ZnS(Ag) and ZnS(Au) belong to the same group and CdS has been substituted for ZnS in part or completely. All these materials are known as 'conventional' crystal phosphors.

In these crystals excitation raises electrons into the conduction band. The greater the concentration of electrons in this band the greater the luminescence and the photoconductivity. A marked photoconductivity occurs showing parallel behaviour to the emission both during excitation and decay. This parallel behaviour is qualitative since the conduction electron density is not the only factor which influences the two phenomena: photoconduction also depends on the electron mobility and charge distribution, &c., while luminescence depends on the number of empty recombination centres and the radiative transition probability, &c. The comparative study of the two effects does, however, give most useful information.

Another characteristic of conventional sulphide phosphors, the luminescence emission occurs only when conduction electrons recombine with specific impurities or defects known as luminescence centres. It is only when such normal activator impurities are absent that other luminescence effects are observed and only for special conditions such as very low temperatures, e.g. the Ewles–Kröger type of emission and exciton luminescence.

Radiative transitions with visible light emission due to conduction electrons recombining with positive holes in the valence band are not completely forbidden. However, they obey momentum conservation rules which make the transition probability so small that emission is unobservable.

I. THE 'MOMENTUM' SELECTION RULE AND ITS CONSEQUENCES

1. Conservation of momentum in optical transitions from band to band

Consider the optical transition of an electron between two stationary states in the crystal lattice described by Bloch functions:

$$\psi_k = \nu_k \exp{(i\mathbf{k}.\mathbf{r})}$$

for the initial state and

$$\psi_{k'} = \nu_{k'} \exp{(i\mathbf{k}'.\mathbf{r})}$$

for the final state. $\mathbf{k}$ is the reduced wave vector, i.e.

$$k = \frac{mv}{\hbar} = \frac{2\pi}{\lambda}, \qquad \mathscr{E}(k) = \frac{\hbar^2 k^2}{2m}$$

where $\mathscr{E}(k)$ is the kinetic energy of the electron. For approximation to free electron conditions, ν_k and $\nu_{k'}$ will modulate the exponential factor with the 'periodicity' of the lattice.

The matrix element corresponding to absorption or emission of a photon of wave number q is

$$H_{kk'} = \int \psi_{k'}^{*} \frac{e}{2mc} \frac{\hbar}{i} (\mathbf{A}.\mathbf{grad})\psi_k \, d\tau$$

$\mathbf{A}$ is a vector potential of the form

$$\mathbf{A} = \alpha \exp{(\pm i\mathbf{q}.\mathbf{r})}$$

α being a vector orientated in the direction of polarization.

$H_{kk'}$ can be written

$$H_{kk'} = \int \exp{[i(\mathbf{k}-\mathbf{k}'\pm\mathbf{q}).\mathbf{r}]}(\nu_{k'}^{*}X\nu_k) \, d\tau$$

where $(\nu_k^{*}X\nu_k)$ represents a quantity which need not be explained but has the periodicity of the crystal lattice. It follows that

$$H_{kk'} = \sum_{R_m} \exp{[i(\mathbf{k}-\mathbf{k}'\pm\mathbf{q}).\mathbf{R}_m]}$$

$$\times \int_m \exp{[i(\mathbf{k}-\mathbf{k}'\pm\mathbf{q}).(\mathbf{r}-\mathbf{R}_m)]}(\nu_{k'}^{*}X\nu_k) \, d\tau$$

where the integral $\int_m$ is extended to the mth cell of the lattice and $\mathbf{R}_m$ is a vector from the origin to a point which represents this cell.

All the integrals $\int_m$ are identical and equal to A and so

$$H_{kk'} = A \sum_{R_m} \exp{[i(\mathbf{k}-\mathbf{k}'\pm\mathbf{q}).\mathbf{R}_m]}$$

On the average† the sum is zero unless the following condition is fulfilled:

$$\mathbf{k} - \mathbf{k}' \pm \mathbf{q} = \mathbf{K}$$

where $\mathbf{K}$ is a principal vector of the reciprocal lattice

$$\exp(i\mathbf{K}.\mathbf{R}_m) = 1$$

This is a generalization for a crystal lattice of the law of conservation of momentum. For absorption we have $+\mathbf{q}$ and for emission $-\mathbf{q}$.

In general, the photon wavelength is large compared with the wavelengths of electrons involved in such transitions (for 1 eV electron $\lambda = 1.22 \times 10^{-7}$ cm) and so for these conditions we have

$$\mathbf{k} - \mathbf{k}' = \mathbf{K}$$

which shows that there is conservation of the reduced wave vector in direct, radiative band-to-band transitions (often called the *momentum* selection rule). In the energy band model such transitions are *vertical*.

2. Discussion

We now consider excitation in the fundamental absorption band of the lattice, i.e. producing a conduction band electron. The electron and hole so produced must obey this selection rule and can immediately recombine. However, the electron will diffuse towards the bottom of the conduction band and the hole to the top of the valence band. The diffusion is due (*a*) to interactions between electrons and (*b*) to interaction of electrons and holes with the crystal lattice.

The second effect (*b*) is usually assumed to predominate. The mean free path of the 'slow' electrons in ZnS is about 10^{-7} cm and the mean velocity about 10^7 cm/sec. Phonon diffusion or scattering of the electrons occurs every 10^{-14} sec. Thermal equilibrium between the electrons and the lattice can be attained in 10^{-12} to 10^{-10} sec, a time which is much smaller than the life time for radiative dipole transitions (10^{-8} sec). It is the rapidity of this diffusion which in semiconductors allows us to introduce the idea of 'quasi-Fermi levels'.

The effect (*a*) above only occurs if there is a large concentration of conduction electrons (10^{-14} e/c.c) already.‡ This can be the case for

† We often say – a little too hastily – that the matrix element is zero in order that the above conservation law is justified. Actually the summation included in the expression for $H_{kk'}$ is rarely zero. It oscillates about zero while remaining finite. When we normalize by dividing by the crystal volume we obtain a quantity tending to zero for an infinitely large volume and then the conservation rule is justified.

‡ Cf. J. Bok, Thesis, Paris, 1959.

intense ultra-violet excitations or excitation by particles. A distinct difference in temperature between the electrons and the crystal lattice is therefore not impossible due to the continued arrival of energetic electrons in the band. This possibility was considered in 1938 by Birus and Schön.

Whatever the cause of electron diffusion, once it has occurred the electron and positive hole do not show identity of momenta and so cannot recombine with photon emission. They can, however, recombine with simultaneous emission of a photon and a phonon, the latter carrying away the excess momentum but with small energy. This effect is well known for germanium, where it is assumed to be responsible for the infra-red emission at about 0·68 eV ($\lambda \approx 1·8\ \mu$) obtained for high carrier densities. An analogous process is not impossible in zinc sulphide. However, this recombination process has a long life time of about a second, and in sulphides with activators is masked by recombination and emission of the luminescence centres, apart from non-radiative transitions in defects. Even in germanium it only appears for carrier concentrations of $\approx 10^{19}$/c.c due to injection of a dense flux of electrons and holes. At lower concentrations recombinations occur in defects which are in general non-radiative (deathnium).

We now return to the case of direct band-to-band transitions solely with photon emission, which is highly likely if after diffusion the electron and hole have the same reduced wave vector. This is so if the conduction and valence bands have their minima and maxima respectively at a wave vector value $k = 0$ (see Fig. IV.1).
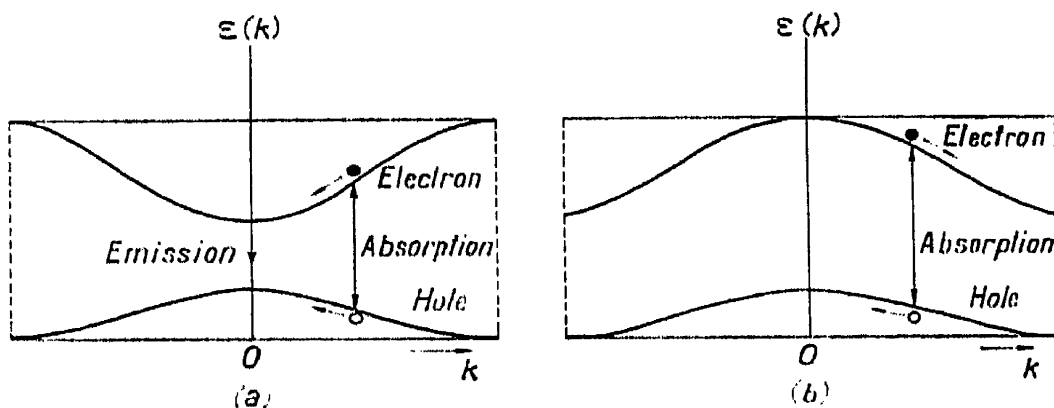
Fig. IV.1

(a) *Band structure allowing direct vertical band-to-band transitions with light emission (photon emission only)*
(b) *Band structure with such transitions forbidden*

However, energy band structures are more complex than that in Fig. IV.1. Fig. IV.2 shows the schematic energy band diagrams (k) for germanium (Herman) and indium antimonide (Kane and Dresselhaus) respectively.
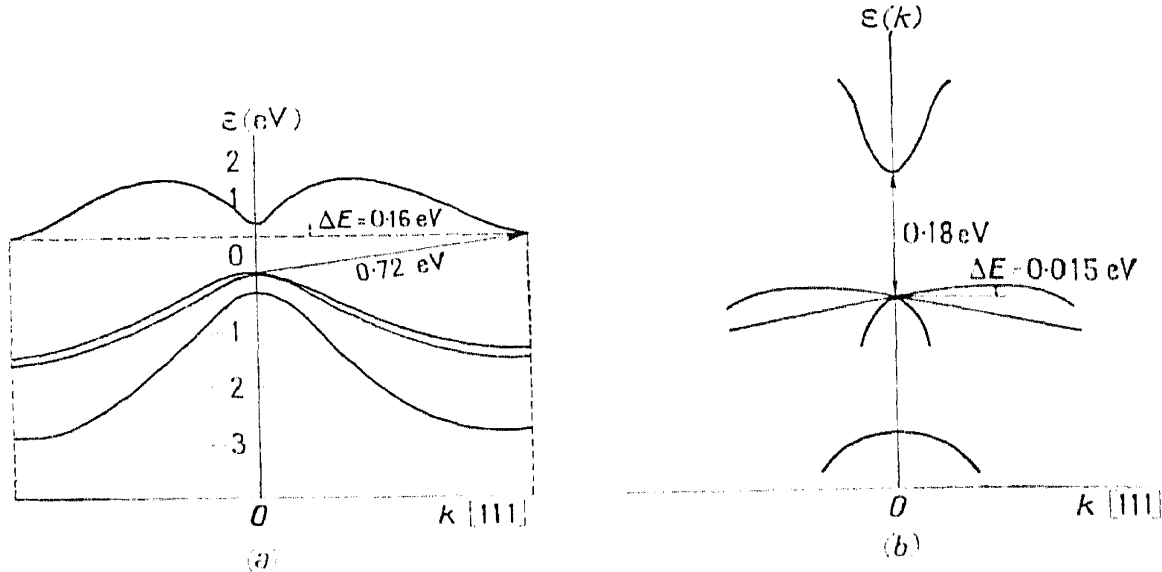
Fig. IV.2

(a) Energy band structure for germanium (after Herman)
(b) Energy band structure for indium antimonide
(after Kane and Dresselhaus)

In germanium the conduction band has a minimum at $k = 0$ but also eight equivalent minima situated at the band extremities along the (111) directions (and thus only four different minima are observed) and lower by $\Delta E \approx 0.16$ eV than the first minimum. The valence band maximum is at $k = 0$ but is complex. In indium antimonide the conduction band has a minimum at $k = 0$ but the vallnce band in addition to a maximum at $k = 0$ has eight equivalent maxima along the (111) directions close to the origin and higher than the first maximum by $\Delta E \approx 0.015$ eV.

In such systems there are no vertical, radiative transitions (without phonons) at low temperatures. Only the lowest conduction band minimum and the highest valence band maximum are populated with electrons and holes respectively, and these do not have the same wave vectors (see Fig. IV.16). However, at higher temperatures (such that $kT \approx \Delta E$) the populations at the value $k = 0$ become appreciable and there is a probability of direct radiative transitions which grows with temperature thus:

$$P_{\text{rad}} \approx \exp\left[-\frac{\Delta E}{kT}\right]$$

TABLE IV.1

Value of the energy gap for some semi-conductors at different temperatures

	4°K (eV)	77°K (eV)	291°K (eV)
Germanium	0·74	0·72	0·65
Silicon	1·14	1·13	1·08
InSb	0·23	0·22	0·18
ZnS blende	3·77	3·75	3·64
ZnS wurtzite	3·83	3·81	3·70
CdS wurtzite	2·55	2·52	2·43
SiC hex.	2·92	2·91	2·86

In the case of zinc and cadmium sulphides we do not have evidence, such as was obtained from the 'cyclotron resonance', magneto-resistance and magneto-optical experiments which lead to the above schemes in the case of germanium and InSb. However, the study of the optical absorption allows us to make some reasonable assumptions. It seems that both valence and conduction bands possess extrema at the origin $k = 0$ or very close to it, but probably not the 'minimum minimorum' of the conduction band or the 'maximum maximorum' of the valence band. Thus the long wavelength limit of the fundamental absorption band is probably due to phonon-assisted transitions, as for Ge and InSb. The energy of direct vertical transitions is higher by a few tenths of an electron-volt.

The conduction band is due to s-states of the Zn or Cd ions, and the valence band to s- and p-orbitals of the sulphur ions, more or less hybridized according to the covalent character of the compound (sp^3 orbitals in a purely covalent Pauling model). A small degree of admixture of Zn or Cd levels inside the valence band is quite possible, but it may probably be neglected in the semi-quantitative considerations at present possible.

For CdS more elaborate computations have been made than for ZnS. According to Balkanski and des Cloizeaux the valence band has the following structure:

As a first approximation, the band is divided into three parts. The lowest sub-band derives mainly from s-states of the sulphur ions, and the other two from p-states. The (p_z) orbitals extending along the hexagonal axis are more strongly bound than the (p_x) and (p_y) orbitals. This assumption (Dresselhaus) comes from the fact that the c/a ratio in the CdS lattice is somewhat smaller than its value in the ideal

hexagonal structure:

$$\frac{c}{a} \text{ (hexagonal compact)} = \sqrt{\frac{8}{3}} = 1 \cdot 633$$

$$\frac{c}{a} \text{ (CdS)} = 1 \cdot 623$$

For ZnS, this ratio is very near to the ideal value; the separation between (p_z) and (p_x, p_y) is probably smaller. The value

$$\frac{c}{a} \text{ (ZnS)} = 1 \cdot 637$$

has been given, but the difference from the ideal value is of the order of the experimental errors and thus not significant.

To a second-order approximation, the spin-orbit coupling lifts the degeneracy of the upper valence band. The states for which the spin is parallel to the orbital momentum (Γ_9 symmetry) have a higher
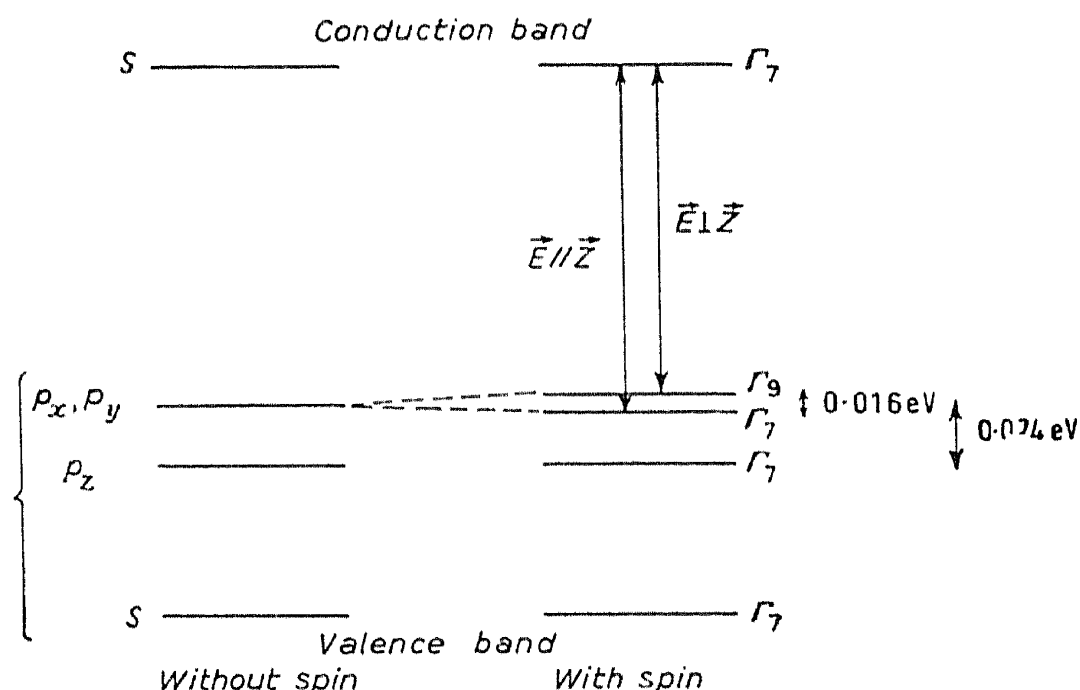
Fig. IV.3 *Structure suggested for the valence and conduction bands of CdS according to Balkanski and des Cloizeaux*

energy than the states for which the spin is antiparallel (Γ_7 symmetry).

This structure of the valence band results in a structure in the long-wave limit of the fundamental absorption spectrum. With polarized light the absorption transition between the Γ_9 levels and the conduction band is observed with light polarized perpendicularly to the optic axis, and the transition arising from the Γ_7 levels with light polarized

parallel to the optic axis. The energy difference between the two transitions is 0·016 eV in CdS (Balkanski and Waldron).

The same structure is observed in studies of the maximum of the photoconductivity excitation spectrum. Bube has shown that this
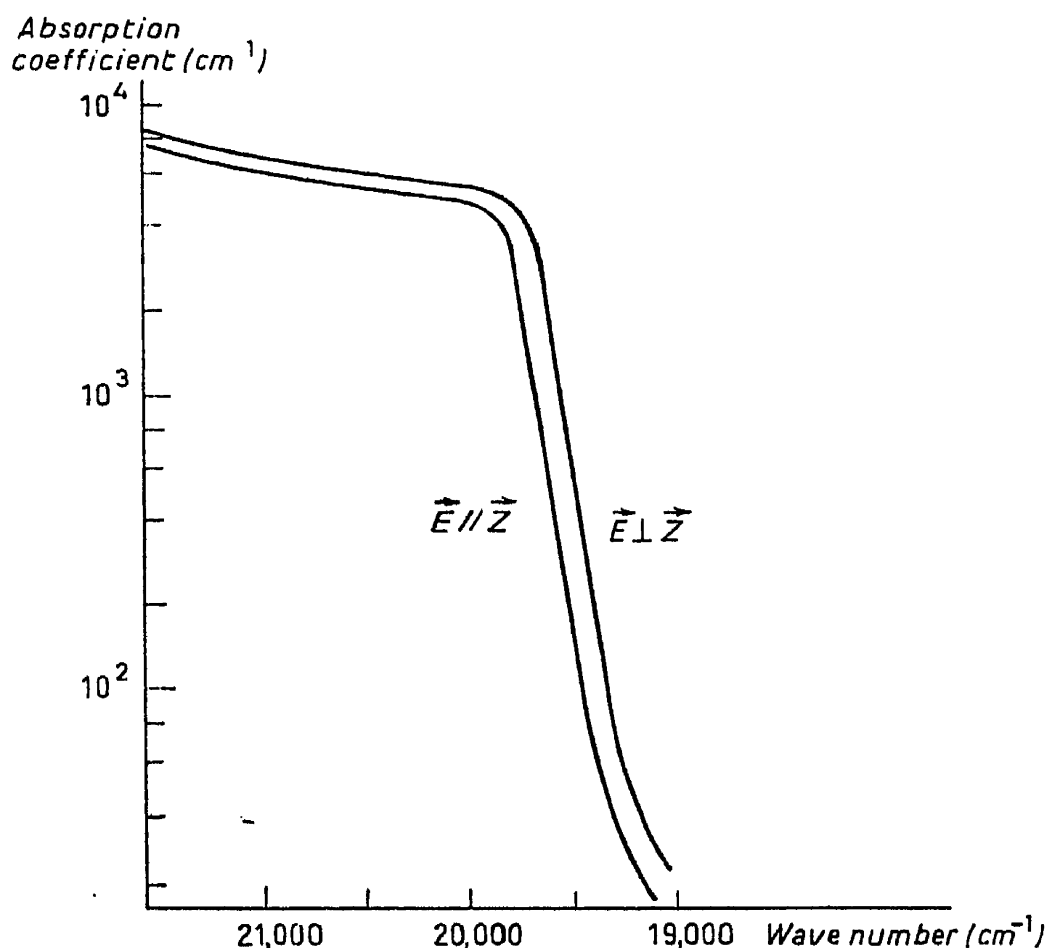
Fig. IV.4 *Absorption spectrum of monocrystals of cadmium sulphide* (*Balkanski and Waldron*)

E is the electric field of the radiation and z the optic axis of the crystal

(*Measurements at room temperature*)

maximum is divided into two components whose separation is 0·017 eV in CdS and 0·015 eV in CdSe respectively.

An absorption band has been observed in the infra-red, at 17 μ (0·074 eV) in CdS, and ascribed by Balkanski and co-workers to the transition between the (p_z) and (p_x, p_y) sub-bands.

The s part of the valence band is much lower, possibly 1 eV lower. It has been suggested (G. Curie) that infra-red stimulation and quenching bands, which appear in all sulphides at 1·3 μ for ZnS and 1·4 μ for CdS, be ascribed to a transition inside the valence band,

leading from the *s*-states to one of the *p*-states. The possibility of such a transition depends on the occupation of these different levels, which may be sensitive to the incorporation of the activator, but this point is not yet resolved.

II. LUMINESCENCE EMISSION NEAR TO THE ABSORPTION EDGE ('EDGE EMISSION')

1. Spectra for electron-positive hole recombination in germanium

Near a *P–N* junction it is possible to obtain considerable electron and hole concentrations ($\approx 10^{19}$/c.c). Radiative recombination of the electrons and holes is observed. As seen above, there must arise non-vertical transitions in the band diagram except at sufficiently elevated temperatures. The width of the forbidden band being about 0·72 eV at 77°K (see Fig. IV.2), an emission band is observed in the infra-red region at 1·8 μ.

At liquid air temperature we find only this phonon-assisted transition. When the experiments are carried out at room temperature or above it is possible to detect in addition a peak at 0·81 eV (1·5 μ) (Haynes) which is ascribed to vertical transitions without phonon cooperation at $k = 0$. The energy of this second peak is equal to the sum $E_{gap} + \Delta E$, where $E_{gap} = 0·65$ eV at room temperature and $\Delta E = 0·16$ eV (see Fig. IV.2). Its intensity increases with temperature, the activation energy being ΔE. However, this radiation is strongly reabsorbed, and is observed only when very thin specimens are used.

Using the law of detailed balancing, Shockley and van Roosbroek obtained the recombination emission probability. If $\rho(\nu)$ is the radiation intensity for a black body

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1}$$

The intensity of emission per second and per electron hole pair in the frequency band ν to $\nu + d\nu$ is

$$I(\nu)\, d\nu = \text{const. } k(\nu)\rho(\nu)n^2(\nu)\, d\nu$$

where $k(\nu)$ is the measured absorption coefficient and $n(\nu)$ the refractive index at frequency ν.

This calculation gives the life time for the recombination emission. This is about 0·75 sec at ordinary temperatures. The observed life time due to recombination via defects rarely exceeds 1/100 sec,

showing that direct recombination is a relatively rare event. This is why it is only observed in cases of high carrier concentrations.
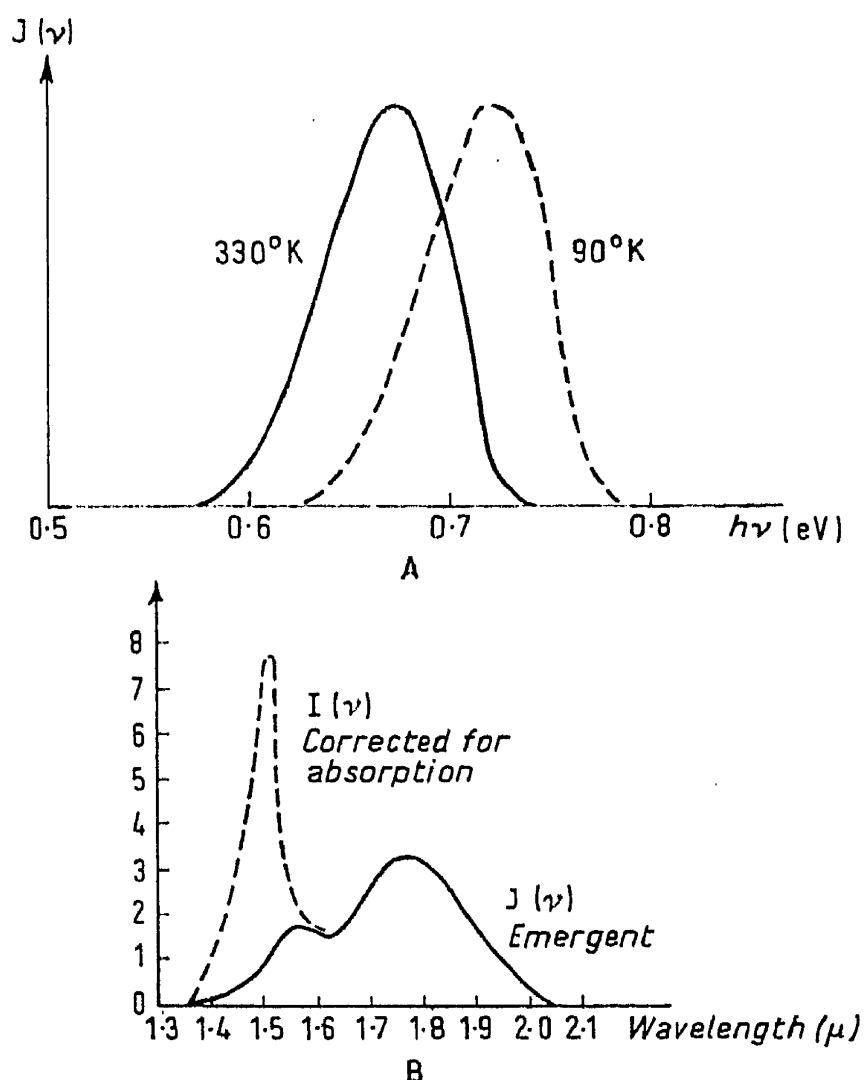
Fig. IV.5 *Emission spectrum due to band-to-band recom-bination in germanium*

A *Experiments by Aigrain and Benoit à la Guillaume*
B *Experiments by Haynes performed on a very thin sample* ($l = 1·3 . 10^{-3}$ *cm*)

The form of the emission spectrum is also determined by the re-absorption of the emitted radiation: if l is the dimension of the emitter, the radiated energy is given by

$$J(\nu) \propto \int_0^l I(\nu)e^{-k(\nu)x} \, \mathrm{d}x$$

This integral depends on the geometry of the specimen. If the emission originates at a point then $J(\nu) = I(\nu)e^{-k(\nu)}$. If the recombination

D

takes place uniformly throughout the sample thickness *l* (experiments of Haynes and Newman), then

$$J(\nu) = I(\nu)\frac{1-\mathrm{e}^{-k(\nu)l}}{k(\nu)l}$$
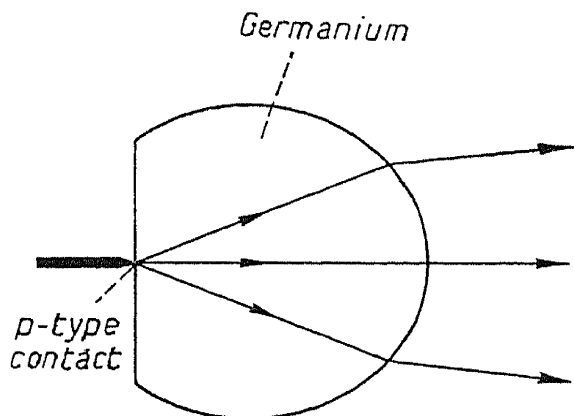
Fig. IV.6 *Weierstrass sphere made of germanium (P. Aigrain and C. Benoit à la Guillaume): injection is made at the Weierstrass point which minimizes the light losses*

The maximum corresponds almost exactly with the width of the forbidden band, since at longer wavelengths it falls off rapidly according to Kirchhoff's law and since at shorter wavelengths than that of the absorption edge the photons are strongly reabsorbed.

In silicon the energy band gap is 1·08 eV and a recombination emission is observed at 1·2 μ.

Haynes found a structure in this emission consisting of four peaks due to the radiative transition emission coupled with longitudinal or transverse phonons of the acoustic and optical branches respectively.

2. Spectra of the Ewles–Kröger type

These emission spectra are observed at low temperatures in ZnS, CdS and ZnO containing no deliberate impurity activators (Fig. IV.7). The luminescence shows a characteristic fine structure (narrow equidistant bands, better resolved at low temperatures) which occurs near the fundamental absorption edge. The effect is most noticeable in CdS, which has an edge in the visible region, a very brilliant green luminescence being seen.

In an activated phosphor the Ewles–Kröger emission is suppressed and that usually due to the activator occurs. The line spacing in CdS is 296 cm^{-1}.

In some cases a substructure occurs of feeble lines with the same separation as the main set, but compared with it, shifted towards the high energy side, by 200 cm^{-1} in CdS.

This is the first known case of edge emission, but it seems certain that it is not due to band-to-band transitions. The emission always has a smaller photon energy than the band gap energy ($\approx$ 0·15 eV as in Fig. IV.7). It is thought that it is due to the recombination of a hole

with an electron captured in a level of 0·15 eV depth, a theory first proposed by Schön.

This 'shallow' level is not very localized and has an associated vibrational frequency near to but not exactly that of the phonons of the
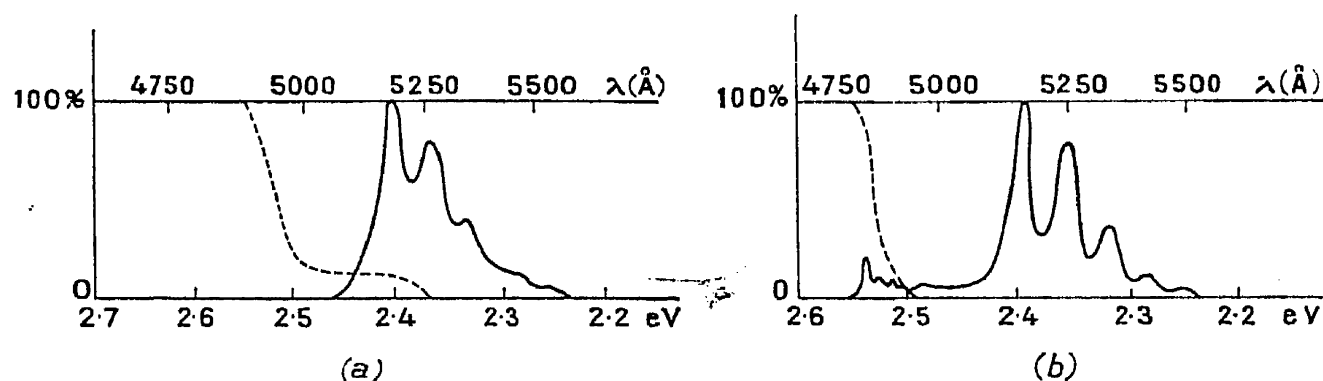
Fig. IV.7 *Ewles–Kröger spectra of a single crystal of cadmium sulphide (after Klick), (a) at 77°K (b) at 4°K*
(*The full curves give the emission, broken curves the absorption spectra*)

perfect lattice. Kröger and Meyer have taken the line spacing of the principal emission lines to correspond to the frequency of the longitudinal optical phonons and that of the substructure to correspond to the frequency v_t of the transverse optical phonons.

For the case of ZnS (blende), the best measurements of these frequencies v_l and v_t are given by studies on infra-red absorption and Raman Spectra (Mme L. Couture, M. C. Haas and J. P. Mathieu). For CdS and ZnO we have the measurements on 'Reststrahlen' by R. J. Collins. In every case, the interval Δv between the main lines

Fig. IV.8 *Ewles–Kröger emission*
(*After Schön*)

of the emission spectrum is slightly different from v_l, but the discrepancy seems real.†

Hopfield (1959) has shown that the heights of the different peaks

† Quite recently, Choyke, Hamilton and Patrick (1960) have described edge emission phenomena in SiC which seem to indicate electron-hole recombination occurring in donor-acceptor pairs. The separation (0·03 eV) of the lines is here quite different from the energy of the optical phonons (0·09 eV for transverse phonons and 0·12 eV for longitudinal phonons). For a description of other luminescence emission shown by SiC, see Chapter IX, §II.3.

TABLE IV.2

| | ZnS | | CdS | ZnO | |
	Blende	Wurtzite	Wurtzite	Hex.	
$\Delta\nu$	364	368	296	550	cm^{-1}
ν_l	349	?	305	591	cm^{-1}
ν_t	274	?	241	414	cm^{-1}

are conveniently described by a Poisson distribution. The first emission line I_0 is ascribed to electron-hole recombination leading to the emission of one photon and no phonon, the second line I_1 to a photon accompanied by one phonon, the $(n+1)$th line I_n to the simultaneous emission of the photon and n phonons. The respective intensities are

$$I_n = I_0 \frac{N^n}{n!}$$

where N is the mean number of emitted photons. In CdS a fit is obtained with $N = 0.87$.

TABLE IV.3

Number of phonons	Relative peak height
$n = 0$	1.00
1	0.87
2	0.38
3	0.11
4	0.03

Polarization of the edge emission. The emission is mainly polarized with $E \perp z$ (E the electric field of the radiation, z the optical axis of the CdS crystal). At 77°K (Dutton, Hopfield and Collins)

$$\frac{I_\perp}{I_\parallel} = 6.3$$

In ZnO the polarization is almost total.

These results are in agreement with the structure of the absorption limit as described in Fig. IV.4 if we admit that the shallow level responsible for the edge emission possesses the same symmetry as the conduction band. If ΔE (0.016 eV in CdS) is the separation between the Γ_9 and Γ_7 levels in the valence band, the polarization ratio is

$$\frac{I_\perp}{I_\parallel} \simeq \exp\left(\frac{\Delta E}{kT}\right)$$

In CdS the approximate theoretical value is 7.

Other experiments are necessary in order to identify this shallow level. F. E. Williams has suggested that it be considered as a level of an electron trapped in the field of an electric dipole constituted by

two associated vacancies acting like substitutional charges of opposite signs. Some proof of this hypothesis has been given by L. Patrick for the case of SiC. Indeed, it seems most probable that the edge emission must be ascribed to physical defects in the lattice (vacancies or interstitial atoms) rather than to chemical impurities.

This idea is supported by the fact that so many people have made experiments on the incorporation of chemical impurities in zinc or cadmium sulphides that, if one of these impurities had been responsible for the Ewles–Kröger spectrum, someone would certainly have found it. The experiments of Kulp and Kelley, described in Chapter X (page 309) indicate quite definitely the occurrence of vacancies or interstitials. Edge emission appears on bombardment by accelerated electrons, when the energy of these electrons is higher than the threshold for S-vacancy production.

As a general rule, the emission that occurs at the band edge seems to be dependent on the surface condition of the crystal (D. C. Reynolds). It is destroyed by scraping the surface (but it is restored by etching). This result does not prove that the edge emission occurs at the surface, but more probably that scraping produces defects acting like 'killer' centres.

We notice also in Fig. IV.7 the appearance at 4°K of a spectrum in the blue region which also shows structure. This spectrum (non-hydrogenlike) has been observed by various workers (Kröger, Klick, Arkhanguelskaia and Feofilov, Furlong and Ravilious). It is found at the fundamental absorption edge but differs from exciton spectra which had been in question. It arises from superficially absorbed impurities.

The Ewles–Kröger spectrum is usually obtained by photo-excitation. However, it was obtained by R. W. Smith by injection of electrons and holes into unactivated cadmium sulphide using indium electrodes. In the Ewles–Kröger spectrum observed only at low temperatures a second emission band was superimposed nearer to the absorption edge which appeared to be due to direct electron-hole recombination: this band persisted at room temperature and above (see Fig. IX.15).

In a remarkable experiment, the excitation of the Ewles–Kröger spectrum has been produced by infra-red excitation (Halsted, Apple and Prener, 1959). This result is a marked violation of the Stokes rule. It is explained by a two-stage excitation process.

A CdS sample containing copper is used. The concentration of copper is rather low and the edge emission is not suppressed; however, the copper levels play a fundamental part in the excitation pro-
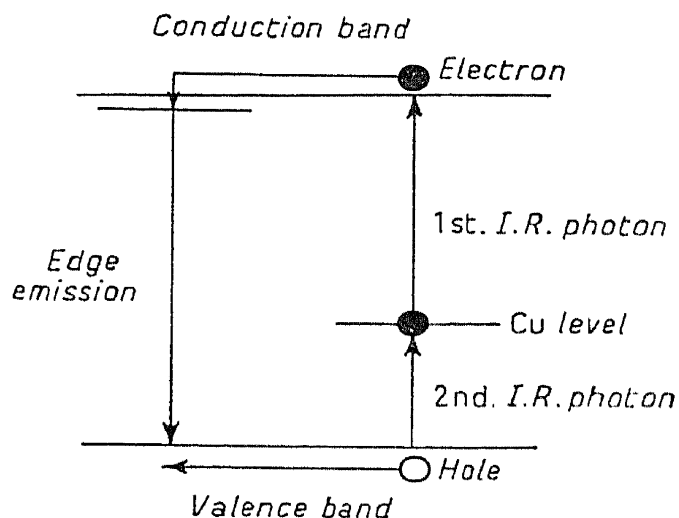
Fig. IV.9 *Two-stage excitation of the edge emission* (*Halsted, Apple and Prener*)

cess. The first infra-red photon ionizes the Cu-level into the conduction band; the second one raises an electron of the valence band into the copper level. Then this level is filled again, while a free electron-hole pair has been produced. Their recombination produces the green emission (and also, of course, the infra-red emission associated with copper).

III. ABSORPTION SPECTRA AND EXCITON EMISSION

1. The experimental evidence

In recent years Gross, Nikitine and their co-workers have found in Cu_2O, CdS, HgI_2, AgI, PbI_2, &c., series of absorption lines appearing near the absorption edge and which can be represented by a hydrogenlike formula. The lines can be interpreted as the optical spectra associated with the creation of excitons.

Since 1956 homologous line series have been found in emission from the same materials. They were first observed in CdS but with layers prepared in a special way.

These crystals, deposited by sublimation at relatively low temperatures (700°C), are assumed to contain few defects. They show a very weak Ewles–Kröger luminescence in the green region, but the exten-

sion into the blue appears to be absent and is replaced by a series of quasi-hydrogenlike lines (E. and M. Grillot, Pesteil and Zmerli). Lines of the same kind were observed for HgI_2, PbI_2, AgI and CdS by Arkhanguelskaia and Feofilov, Nikitine, Perny, Reiss and Sieskind. They obtained a detailed spectrum for AgI and numerous lines in the other cases investigated.

Whether in absorption or emission these spectra are observed at low temperatures; at higher temperatures the lines broaden and merge into the absorption tail. Thin layers are needed for the experiments (one to a few tens of microns, depending on the line intensities) and they must be free from defects.

2. Theoretical aspects

From a theoretical point of view the exciton was first thought of as a neutral *excitation wave* capable of movement through a crystal (Frenkel, 1930): in recent years this idea has received new interest, correlated with studies of exciton transfer (see later). Then in 1938 Wannier established the quasi-hydrogenlike character of the levels produced while Mott, Slater and Shockley described the exciton as an electron in orbit around a hole bound to it by the coulombic attraction.

In the excitation-wave model the formation of an exciton in KCl corresponds to the movement of an electron from a Cl^- ion to one of the neighbouring K^+ ions while excitation of an electron from the valence band (Cl^-) to the conduction band K (see Fig. II.2) corresponds to a complete freeing of the electron in the body of the crystal. The calculation of the energy cycle analogous to those made to find the forbidden energy gap enabled von Hippel, J. de Boer *et alia* to find the energy for exciton formation. Thus the width of the forbidden band in KCl is 9·42 eV, giving an optical absorption edge at 1,310 Å, while exciton formation requires only 7·6 eV, giving a first absorption peak at 1,620 Å. We thus obtain the first exciton state.

In a similar way for CdS the first exciton state corresponds to the transit of an electron from a sulphur ion (i) to one of the neighbouring cadmium ions (M) (M. Balkanski and P. André). However, the wave function obtained from that of the matrix crystal by replacing that for the sulphur ion by the Hartree function for this ion containing a positive hole and replacing that of the cadmium ion M by the Hartree function for this ion with an excess electron, say $\phi(i, M)$,

is not an eigenfunction of the crystal. For the eigenfunction a wave packet of the $\phi(i, M)$ functions must be taken:

$$\psi \text{ (for crystal containing exciton)} = \sum_{i,M} A_{i,M} \phi(i, M)$$

It is possible to take A coefficients of the form

$$A \propto \exp(i\mathbf{k} . \mathbf{R})$$

$\mathbf{R}$ locates the exciton and $\mathbf{k}$ plays the part of a propagation vector. Near to the limit $\mathbf{k}_0$ we can obtain the energy

$$\mathscr{E}(\mathbf{k}) = \mathscr{E}(\mathbf{k}_0) + \frac{\hbar^2}{2} \frac{1}{M} k'^2 + \cdots$$

where $\mathbf{k}' = \mathbf{k} - \mathbf{k}_0$, this corresponding to the motion of an exciton with effective mass M.

This model is preferable for calculating the ground state and transitions involving this state and more generally for the case where the electron 'orbit' around the hole is of small radius. This is so for the alkali halides because of their relatively small dielectric constants (Slater and Shockley, T. Muto and Okuno).

3. Model for the electron in orbit around a hole; hydrogenlike spectra

In contrast to the above the model for an electron orbiting about a hole, called the 'quasi-positronium' model, gives a direct explanation of the hydrogenlike spectra for the excited state.

Let m_e and m_h be the effective masses for conduction electrons and holes in the valence band respectively, the bands being isotropic and for non-degenerate conditions. The Wannier equation for the exciton is then

$$H\psi = E\psi$$

$$H = -\frac{\hbar^2}{2m_e}\Delta_e - \frac{\hbar^2}{2m_h}\Delta_h - \frac{e^2}{Kr}$$

K being the dielectric constant of the material. Let $\mathbf{r}_e$ be the electron co-ordinate, $\mathbf{r}_h$ that of the hole and $\mathbf{R}$ that of the centre of gravity:

$$\mathbf{R} = \frac{m_e \mathbf{r}_e + m_h \mathbf{r}_h}{m_e + m_h}$$

The equation has solutions of the form

$$\psi(\mathbf{R}, \mathbf{r}) = \exp(i\mathbf{k}\mathbf{R})\psi(\mathbf{r})$$

corresponding to a motion of the centre of gravity with wave vector $\mathbf{k}$. It is easily shown that $\psi(\mathbf{r})$ is a solution of the hydrogenlike

equation

$$-\frac{\hbar^2}{2\mu}\Delta\psi(r)-\frac{e^2}{Kr}\psi(r) = \mathscr{E}\psi(r)$$

$$E = \frac{\hbar^2}{2M}k^2+ \mathscr{E}; \qquad M = m_e+m_h$$

M is the effective mass of the moving exciton and μ the reduced mass

$$\frac{1}{\mu} = \frac{1}{m_e}+\frac{1}{m_h}$$

The energies $\mathscr{E}$ form a hydrogenlike series:

$$\mathscr{E}_n = -\frac{R'}{n^2}; \qquad R' = \frac{R}{K^2}\cdot\frac{\mu}{m}$$

R' being a pseudo-Rydberg constant; R is the Rydberg constant for hydrogen (13·5 eV) and m the free electron mass. The electron-hole separation in the orbit nS of the exciton is

$$a_n = n^2 a_0', \qquad a_0' = Ka_0\frac{\mu}{m}$$

(a_0 is the Bohr radius = 0·53 Å).

For a given $\mathscr{E}$ there is a corresponding energy band, the total energy of the exciton being $\mathscr{E}$ plus the translational energy $\hbar^2k^2/2M$.

In general, we can only expect to obtain weak absorption tails, only the limits of which form a series.

However, in contrast we get a series of hydrogenlike lines when m_e, m and K are isotropic and for vertical transitions at $k = 0$, or more generally for a k value which is the same for a maximum or minimum for the valence and conduction bands respectively. This requires a correspondence as shown in Fig. IV.1a. For such a band structure we have in either absorption or emission the lines

$$h\nu_n = h\nu_\infty-\frac{R'}{n^2}$$

$h\nu_\infty$ corresponding to the forbidden band-gap energy (Fig. IV.10).

We can very likely observe the line spectra for more complex band structures such as those proposed for CdS in which the extrema of the bands lie at $k = 0$, but the minimum $k = 0$ of the conduction band is not the lowest minimum. After absorption at $k = 0$ and formation of a free electron hole pair, the electron and the hole will diffuse away from each other and will not normally recombine by a vertical radiative transition. In contrast, after an absorption at $k = 0$ giving a bound electron hole pair, the electron and hole will

diffuse together and the possibility of radiative recombination exists. The problem of determining the band structures which will give rise to exciton line spectra and those which will not is still far from clarification.

When the valence band is divided into several sub-bands, a similar number of exciton line series must appear; each series limit coincides
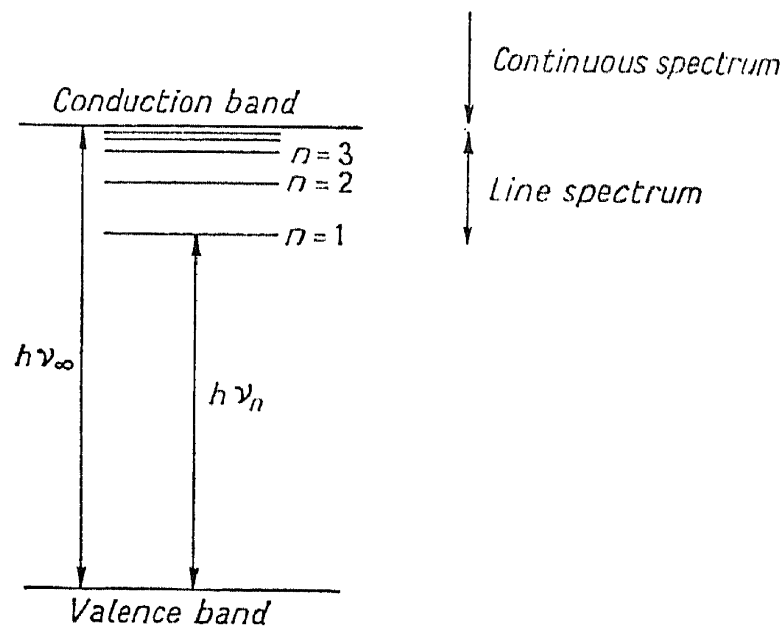
Fig. IV.10 *Energy levels of exciton spectra*

with the transition leading to the ionization of the corresponding sub-level. Two main hydrogenlike series have been observed in Cu_2O (Gross, Nikitine and co-workers): one is situated in the yellow part of the absorption spectrum and is observed with relatively thick specimens (10 to 100 μ); the second series is in the green and is observed with thinner specimens ($\sim 10\,\mu$) because the absorption is stronger in this region.

Since for CdS the upper part of the valence band (p-band) is divided into three sub-levels, we expect three exciton line series in absorption (Balkanski and des Cloizeaux). In emission, these three series might perhaps be observed at a sufficiently high temperature, each of them with a different polarization ratio. At 4°K, the holes are concentrated in the upper Γ_9 level (Fig. IV.3) and the emission is completely polarized ($E \perp z$). This has been effectively shown in experiments (E. and M. Grillot, Gross and Razbirine; Thomas, Hopfield and Power).

Elliott has shown that theory can distinguish two kinds of exciton line spectra:

1. Spectra of the first kind in which transitions for $k = 0$ occur. We observe thus the spectral series for $n = 1, 2 \ldots$ The oscillator strengths are proportional to the squares of the amplitudes of the hydrogenlike wave functions $1s$, $2s$, &c., and are

$$f_n \propto \frac{1}{\pi a_0'^3 n^3}$$

They are weaker than the lines for isolated atoms in the ratio $(a_0'/a_0)^3$, their intensity decreases rapidly with n because of the factor $1/n^3$ and very few lines are observed.

2. Spectra of the second kind in which the transition at $k = 0$ is forbidden but vertical transitions at a constant k value near to zero and leading to p-states are allowed. We obtain in this case

$$f_n \propto \frac{1}{3\pi} \frac{n^2-1}{a_0'^5 n^5}$$

These lines are weaker than the lines for isolated atoms in the ratio $(a_0'/a_0)^5$, but the line intensity falls less rapidly than that for spectra of the first kind and more lines are observed. In all cases the line for $n = 1$ is absent since there is no p-state for $n = 1$.

These deductions are markedly in agreement with experiment (Nikitine *et al.*). Thus CuI shows absorption spectra of the first kind, Cu_2O those of the second kind† and the oscillator strengths show the expected theoretical ratios. The same difference occurs for emission spectra.

When the transition is not vertical and involves a simultaneous emission or absorption of a phonon (as in germanium), line spectra are not observed, but successive knees occur in the absorption curve. At the present time, those knees have been found that are thought to be due to the formation of the ground state of the exciton (Macfarlane *et al.*).

4. Deviations from the hydrogenlike formula

To begin with, the treatment of the exciton in the Wannier equation (called the 'effective mass approximation') makes the crystal a continuous medium of dielectric constant K: this is not valid except for large orbital radii. Also the state $n = 1$ and to a lesser degree the state $n = 2$ may be normally perturbed.

Kittel and Mitchell have used the Wannier equation with a non-isotropic effective mass: Barriol, Nikitine and Sieskind have studied

† The line for $n = 1$ is observed but is very weak.

the anisotropy of the dielectric constant: in both cases the spectra cease to be hydrogenlike.

In an ionic crystal defined by its two dielectric constants K_{static} and K_0 (at high frequencies) it is necessary for a localized level to introduce an 'effective dielectric constant'. However, in the case of the exciton, in absorption ionic polarization has no time to become established in the crystal and it is sufficient to use K_0 in the above calculations.

For emission the problem is more complex. If the electron and hole are very mobile the polarization they produce will be self-destructive and we have a *non-polarizing exciton* (Dykman and Pekar) and again K_0 is used in the calculations. In an ionic crystal only a non-polarizing exciton can give a hydrogenlike emission spectrum corresponding to the absorption spectrum. The observation of such agreement between absorption spectra of CdS obtained by Gross and emission spectra obtained by Grillot is a strong argument for attributing them to excitons since it does not occur for a hydrogenlike impurity (electron in orbit about a fixed positive charge in the lattice, the effective dielectric constant depending on the particular level considered).

If the electron and hole are not very mobile they polarize the surrounding lattice: each of them can be treated as a polaron, i.e. surrounded by an assembly of phonons. In the simplest case we can take account only of the mean value of such polarization (polarizing exciton of Dykman and Pekar), but in general the electron-hole interaction will be modified by their respective surroundings of phonons. For this case we may refer to the work of Haken and of Meyer. Meyer calls such a complex exciton an 'excitaron'.

5. Stark and Zeeman effects for the exciton

These two effects have been studied in Cu_2O by Gross *et al.* and more recently in CdS by E. and M. Grillot in collaboration with Gross. The Stark effect is observed in relatively weak electric fields because of the large size of the exciton orbit. For the hydrogen atom the Stark effect for a field F is

$$\Delta E = -\tfrac{3}{2}neFa_0'   \text{(all } n \text{ values)}$$

for levels of principal quantum number n. a_0' is the radius of the first Bohr orbit, approximately K_0 times greater for the exciton than for hydrogen.

For Cu_2O and $n = 5$ the effect is observed for fields of 5 kV/cm.

Furthermore, we find the phenomenon of ionization of the exciton produced by the shifting of the levels $n = 6, 5, 4$, &c., into the ionization continues as the field increases. The absorption limit is shifted and affects successively each of the terms in the series. For Cu_2O and for $F = 25$ kV/cm only the levels $n = 1$ and $n = 2$ survive. Such an effect for a hydrogen atom requires 600,000 to 700,000 V/cm.

The Zeeman effect for the line $n = 1$ (yellow series of Cu_2O) shows a normal triplet structure. Using the quasi-positronium model, the separation of neighbouring lines is

$$\Delta E = \frac{m_h - m_e}{m_e m_h} \frac{eh}{4\pi c} H$$

We find

$$\Delta E = \frac{eh}{4\pi mc} H$$

if $m_h = \infty$, while if $m_h = m_e$, the linear Zeeman effect is zero. This is well known for positronium: the Larmor procession $\omega = eH/2mc$ produces an enhancement of the electron velocity and a diminution of the positron velocity so that the energy of the system is unaltered to a first approximation. Positronium only shows the quadratic Zeeman effect.

A splitting of terms with $n > 1$ has been observed, but the different components have not been resolved.

The emission lines of CdS also show a Zeeman effect. Sometimes, e.g. that at 4,870 Å, they give the normal triplet. However, the π and σ components are inverted. This suggests a magnetic dipole nature for the emission (E. Grillot) (see Fig. IV.11).
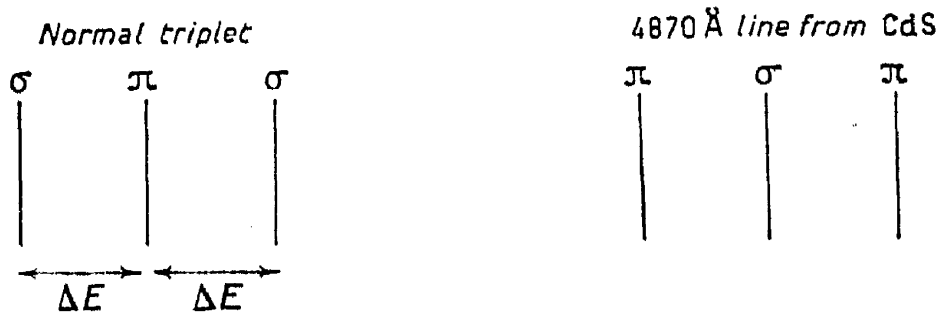
Fig. IV.11 *Normal Zeeman triplet and the inverted triplet obtained by Grillot and Gross for CdS*

With further reference to the lines, a displacement of the centre of gravity of the lines occurs on application of a field H which is quadratic in H. It is explained as a change in magnetic energy due

to the diamagnetism of the exciton. The effect for the n'th level is

$$\Delta E = \frac{e^2}{8mc^2}n^4 a_0'^2 H^2$$

This effect, which only occurs for atoms with higher members of the series, is observed for $n = 3$ ($H = 25$ to 30,000 oersted). The radius $n^2 a_0'$ is of the order of 200 Å for $n = 5$ in the yellow series of cuprous oxide.

In conclusion, experimental evidence reveals the existence of quasi-atomic systems in certain crystals which show hydrogenlike absorption and emission spectra given to a first approximation by the quasi-positronium level system of excitons. The large orbital radii indicated by the Stark and Zeeman effects and the agreement between the experimental and theoretical oscillator strengths strongly support this model, although the theories are often over-simplified and although numerous points still need to be clarified.

The identification of the system responsible for these optical transitions with the Frenkel exciton rests on the evidence of its mobility and its role in energy transfer, which requires other experiments which we shall refer to later (experiments of Broser and of Balkanski on CdS). Light emission due to exciton recombination would seem to be more likely once the exciton has been immobilized in the neighbourhood of a lattice defect.

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Luminescence Centres in

Phosphorescent Sulphides

I. CONSTITUTION OF PHOSPHORESCENT SULPHIDES

1. Preparation

To obtain luminescent zinc sulphide the base material must first be obtained as pure as possible. To do this several methods are available:

(*a*) Hydrogen sulphide is passed through a solution of zinc salt, the zinc sulphide precipitated, washed and dried in an oven.

(*b*) Guntz and Grillot used as the sulphuretting agent sodium thiosulphate $Na_2S_2O_3$ instead of H_2S which forms a disulphide ZnS_2 which is unstable and decomposes to give ZnS at high temperatures.

(*c*) Coustal used a direct reaction of the elements zinc and sulphur, an explosive process but one appropriate for the production of so-called 'self-activated' sulphides.

As necessary a salt of the activator impurity is added in a suitable quantity and often also a flux (e.g. 1 per cent NaCl) and the whole is usually fired at 900°–1,200°C.

If the firing takes place at a temperature below 1,020°C the zinc sulphide crystallizes in the cubic form (blende), above 1,020°C the hexagonal form (wurtzite) is produced. Cooling must be sufficiently rapid to have the wurtzite form persisting at room temperature.

Lewchin has found wurtzite to be present in ZnS made at much lower temperatures ≈ 650°C.

The small difference between the properties of the two forms of zinc sulphide is remarkable. The emission bands are very similar; for ZnS(Cu) the green-band maximum is a little displaced towards the yellow-green in the case of blende crystals, in agreement with the slightly smaller energy-band gap for this form. Both forms show phosphorescence (they appear to have the same groups of electron traps with additional groups in the case of wurtzite). The difference

between the fundamental or lattice absorption edge positions is also very small. In both structures the nearest neighbour configuration is the same, i.e. a tetrahedron of sulphur ions around a zinc ion (or vice versa).

The preparatory methods for cadmium sulphide are analogous, but only the hexagonal form (wurtzite) usually occurs. The blende form has been observed, but only in exceptional cases.

The study of crystalline transformations in ZnS is generally made by optical microscopy using polarized light: hexagonal crystals are birefringent, while cubic crystals are not. This method is an excellent one and was used by A. Guntz as early as 1923. Diffraction experiments by means of X-rays have also been performed. More recently, an interesting method has been proposed by van Wieringen (1953) and used by Aven and Parodi (1960) in order to study the influence of activator impurities (Cu, Ag) on crystal structure. A fraction of about 10^{-4} Mn^{2+} was added to the sample and electron spin resonance studies were carried out. It is well known (page 124) that the resonance spectrum of Mn^{2+} embedded in an hexagonal sulphide possesses 30 lines but only 6 in the blende case.

The energy difference between the blende and wurtzite forms is certainly extremely small; perhaps the transition temperature, and moreover the rate of the transition, is affected by low concentrations of copper. According to Aven and Parodi, heating for one hour at 1,100°C achieves the transformation blende-wurtzite for a concentration of copper $c < 2 \cdot 5 . 10^{-4}$, while the blende structure persists if $c > 7 \cdot 5 . 10^{-4}$. Manganese produces an analogous effect (Kröger) but at larger concentrations.

Addamiano and Aven suggest that the transition temperature for very pure crystals is higher than the accepted value of 1,020°C.

The occurrence of the phase change wurtzite-blende needs nucleation effects whose optimum temperature lies between 700°C (Aven and Parodi) and 900°C (Kremheller). These results seem in agreement with Lewchin's experiments.

2. Numerical values of the energy-band gap for phosphors of the ZnS type

The following table is taken from the review by Bube (*Proc. I.R.E.*) and gives the values for the fundamental optical absorption limit λ_{lim} as well as those for the equivalent quantum energy $h\nu_{lim}$. This quan-

tum is near to the value E for the forbidden band width but more precisely we have

$h\nu_{lim} = E_{gap}$ if the transition is vertical (no phonons involved)

$h\nu_{lim} = E_{gap} - E_{phonon}$ if the transition is effected with simultaneous phonon absorption.

The table also gives the value for the slope β of the curve $E_{gap}(T)$ against temperature T between liquid air temperature and 130°C.

$$E_{gap}(T) = E_{gap}(0) - \beta T$$

TABLE V.1
Fundamental absorption limits

	λ_{lim} (Å) at 293°K	$h\nu_{lim}$ (eV) at 293°K	β (eV/°C)
ZnS blende	3,410	3·64	?
ZnS wurtzite	3,350	3·70	$5·5 \times 10^{-4}$
CdS wurtzite	5,100	2·43	5×10^{-4}
ZnSe blende	4,770	2·60	7×10^{-4}
CdSe wurtzite	7,115	1·74	5×10^{-4}
ZnTe blende	5,780	2·15	?
CdTe blende	8,710	1·42	4×10^{-4}

The values given are those which occur most often in the literature. However, the absorption edge is not so sharply defined and $h\nu_{lim}$ can only be estimated to 0·1 eV. We often fix the absorption limit as the wavelength for which the absorption coefficient is 100 mm^{-1} (Fig. V.1). The limit is most probably associated with a non-vertical (or
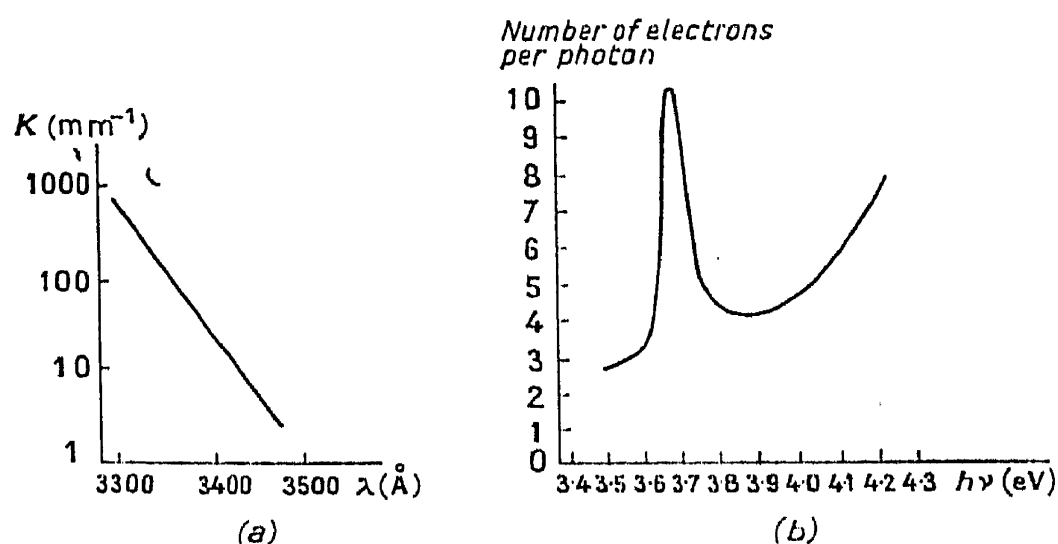
Fig. V.1 *Optical properties of an unactivated ZnS (wurtzite) crystal at room temperature (after Piper)*
    (a) absorption spectrum
    (b) photoconduction response spectrum

indirect) transition (involving phonon absorption) between the valence and conduction bands, the lowest levels of the latter being due to the s-states of zinc or cadmium (Dresselhaus) while the valence band has a more complex structure due to the mixing of the p- and s-states of the sulphur ions. In a purely ionic model for zinc sulphide $Zn^{2+}S^{2-}$ the valence band will be due to the S^{2-} ions while the conduction levels will be those for Zn^{2+} to which an electron has been added, i.e. those for Zn^+ (cf. Fig. II.2 for the monovalent ionic crystal KCl).

The long-wave limit for mixed crystals of ZnS and CdS shifts continuously in the direction of greater wavelengths with increasing cadmium concentration (Henderson, Kröger, Pringsheim). A similar displacement occurs for the luminescence emission bands (A. Guntz, Rothschild, &c.).

This shift is almost linear when the energies $h\nu_{lim}$ are plotted as functions of the percentage of CdS by weight relative to ZnS (Fig. V.2).

This behaviour suggests a small or insignificant difference in the nature of the absorption transition $h\nu_{lim}$ for ZnS and CdS (Kröger). It contrasts with the behaviour of germanium–silicon alloys.
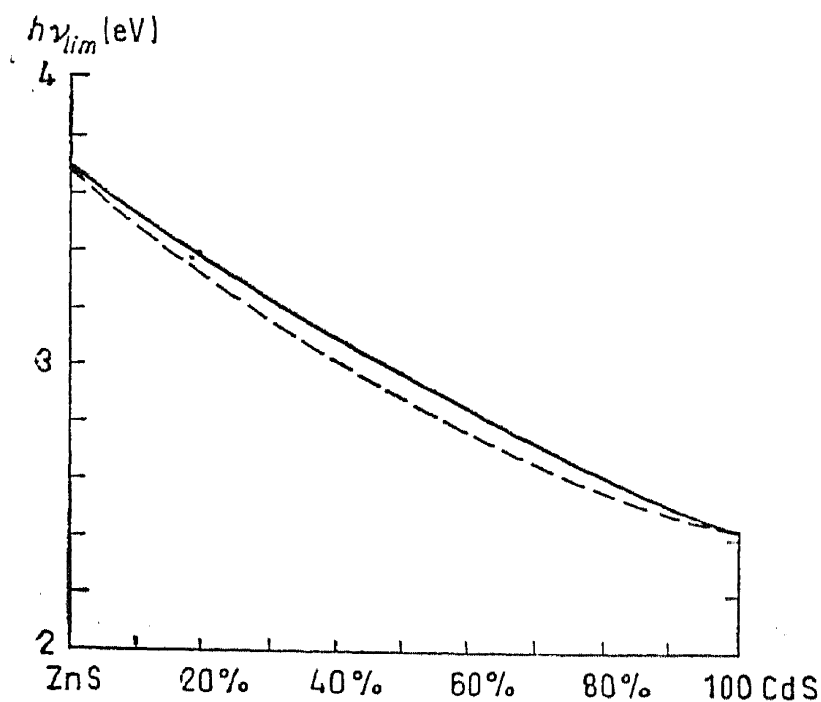
Fig. V.2 *Band gap as a function of composition for zinc–cadmium sulphides*

———— *percentage of CdS by weight*

– – – – – *molar percentage of CdS*

Larach, Shrader and Stocker have shown that the shift is also linear in zinc sulpho-selenides, but strongly concave (with the occurrence of a minimum for an intermediate composition) for ZnS+ZnTe and ZnSe+ZnTe.

3. Observations on the nature of binding in ZnS

The problem of the energy-band structure in ZnS or CdS is, as well stated in a recent work by B. Segall, a formidable computational problem, which implies that the attempts made over several years using considerable means (such as computing machines) are not yet concluded. We may refer to the work of Segall (the Kohn and Korringa method of decomposition into plane waves), that of J. Birman (quasi-cellular method using the effective charge on the ions as a parameter), that of F. E. Williams (quasi-cellular method self-consistent calculation of the electron distribution between zinc and sulphur ions) and that of M. Balkanski (group theory method).

In the meantime we might hope to limit the problem to the possibility of qualitative consideration of the effective ionic charges and of the percentages of ionic binding. However, from many discussions we find that the notion of an effective charge has no unique definition and its introduction in the course of consideration of each problem effectively involves a particular definition. However, such ideas are quite useful if we do not demand too rigorous an approach.

The tetrahedral structure of zinc sulphide is suggestive of a covalent type of binding. While a purely ionic specification would give $Zn^{2+}S^{2-}$, a purely covalent structure would correspond to an equal distribution of the eight valence electrons between the Zn and S atoms and would lead to the charge specification $Zn^{2-}S^{2+}$ (Pauling's 'formal charges').

Coster, Knol and Prins have been able to show by X-ray diffraction studies that the zinc ions are positively charged and the sulphur ions negatively charged. Stretching the blende crystal along the (111) axis would give positive charges on the Zn planes and negative charges on the S planes.

To a first approximation we might place ZnS among the ionic crystals since the static (K) and high-frequency (K_0) dielectric constants are different:

$$K = 8 \cdot 3; \qquad K_0 = 5 \cdot 07$$

The Fröhlich relation between K and K_0 on the one hand and the

wave numbers of the longitudinal and transverse optical vibrations of the lattice ν_l and ν_t respectively on the other hand has been well tested. From J. P. Mathieu *et al.* we have

$$\frac{\nu_l}{\nu_t} = \frac{349 \text{ cm}^{-1}}{274 \text{ cm}^{-1}} = 1 \cdot 274; \qquad \sqrt{\frac{K}{K_0}} = 1 \cdot 280$$

At the same time the parameter $C = \frac{1}{K_0} - \frac{1}{K}$ which occurs in the theory of polarons is, for example, much smaller for ZnS and CdS than NaCl.

TABLE V.2

Table of values for parameter C (Pekar) for various ionic crystals

Crystal	K	$K_0 = n^2$	C
NaCl	5·8	2·33	0·257
KCl	4·78	2·175	0·251
KBr	4·81	2·36	0·217
KI	5·2	2·65	0·185
ZnS	8·3	5·07	0·0767
CdS	11·6	5·85	0·0864
ZnO	12·0	3·88	0·174
Cu_2O	9	4·0	0·139

Although it would be wrong to use C as a true measure of the degree of ionic binding, the small value for ZnS and CdS suggests a marked covalent aspect of binding in these solids. We therefore write the ionic charge as $2e^*$, where e^* is positive but is less than e, and this is the effective charge on the zinc ions.

From measurements of the piezoelectric constant Born and then Saksena have deduced $2e^*$. Born gives $2e^* = 0 \cdot 3e$ and Saksena $2e^* = 0 \cdot 68e$. These values now appear to be too small. Le Corre (1955) took account of non-central forces and the deformation of the ions in a crystal, and from the piezoelectric characteristic deduced $2e^* = 1 \cdot 4e$. H. Poulet applied the Szigeti formula:

$$K - K_0 = \left(\frac{K_0 + 2}{3}\right)^2 \frac{(2e^*)^2}{\pi c^2 V M \nu_t^2}$$

where, together with previous notation, c is the velocity of light, V the volume of the unit cell, and M the reduced mass of the zinc and sulphur ion pair. Using the values of all these quantitives the value $2e^* = 0 \cdot 88e$.

The Szigeti formula uses the Lorentz–Lorenz effective field which is only an approximation, but H. Poulet obtained a good agreement between the experimental states for the Raman spectrum of zinc blende and the calculated characteristics using the above value for the effective charge.

We may therefore conclude that a value of the effective charge $2e^*$ of about unity (75 per cent ionic binding) seems to be applicable to ZnS. The ionic character of the binding is probably about the same in CdS, while, as shown by the Pauling tables of electronegativity, this type of binding will decrease when sulphur is replaced by selenium and above all by tellurium.

Remark: Szigeti's formula is a good approximation, but it is still only an approximation. Let us make a comparison with the effective charge of the ions in the alkali halides:

TABLE V.3

	e^*/e
LiF	0·87
NaF	0·93
KCl	0·80
KI	0·69
RbI	0·87

In lectures given in 1959–60 at the University of Paris, N. Inchauspé developed the following point of view: It seems most probable that in a compound such as LiF the real charge of the ions is very little different from e, and thus likely that Szigeti's formula leads to values of e^* that are a little too small. If the same thing holds in ZnS, the effective charge $2e^*$ will be nearer unity than the above value of $0·88e^*$.

II. LUMINESCENCE CENTRES AND EMISSION SPECTRA FOR ZnS AND CdS

Following Piper and Williams (1958), we shall first reproduce the portion of the periodic table of the elements which is relevant to the class of usual semi-conductors and phosphors and to their activating or coactivating impurities.

TABLE V.4

IB	*IIB*	*IIIB*	*IVB*	*VB*	*VIB*	*VIIB*
		B	C	N		
		Al	Si	P	S	Cl
Cu	Zn	Ga	Ge	As	Se	Br
Ag	Cd	In	Sn	Sb	Te	I
Au	Hg					

From this we can deduce that

In silicon and germanium, P, As, Sb introduce donor levels impurities; Al, Ga, In are acceptors.

In SiC, N and P are donors, B and Al acceptors (see Chapter IX, page 261).

In the phosphors of the ZnS type, made by the combination of an element from column IIB and an element from column VIB:

(*a*) the usual activating impurities Cu, Ag, Au substituted for Zn, Cd, Hg are in acceptor positions; it is the same for P, As, Sb substituted for S, Se, Te;

(*b*) Al, Ga, In and the halogens Cl, Br, I are in donor positions.

1. Copper as an activator

From experience it is found that in ZnS copper produces two main emission bands, a green band at about 5,230 Å (2·37 eV) and a blue one at about 4,450 Å (2·79 eV). Bands also occur in the infra-red (Garlick and Dumbleton) and also a red band which is produced by higher copper concentrations and for which groups of copper ions are probably responsible (Froelich). If we introduce increasing amounts of CdS into ZnS phosphors the above bands are shifted. For pure CdS the equivalent of the blue band is now at 0·82 μ (1·51 eV) and that of the green band at 1·02 μ (1·22 eV).

These band shifts contrast strongly with the case of thallium in the alkali halides. While in the latter the luminescence can, to a first approximation, be attributed to interlevel transitions of the Tl^+ ion,
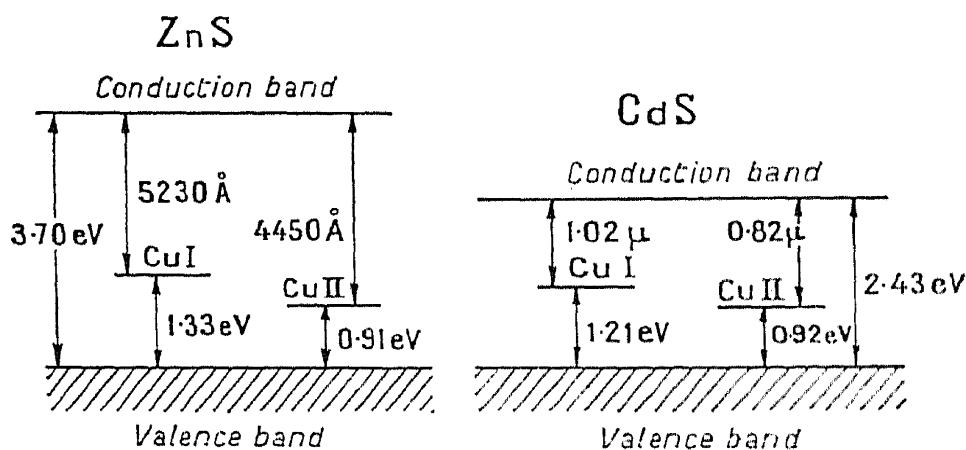

Fig. V.3 *Positions of energy levels giving the characteristic emission bands for copper activator centres in ZnS and CdS (wurtzite)*

Classical level scheme (Riehl–Schön–Klasens)

the interaction with the crystal lattice being treated as a perturbation, in the case of copper activations we cannot identify the transitions with levels of the copper ion. As emission always follows the recombination of a conduction electron with the centre, it is often the practice to represent the centre processes of Fig. V.3 by transitions to their ground states from the bottom of the conduction band. This is rather simplified and we shall see that the emission does appear to involve excited states of the centres at small depths below the conduction band. However, this does not affect the various conclusions below. We see rather that the separation of the centre ground states from the valence band is almost constant, while that from the conduction band alters.† The former is the same for silver-activated ZnS or CdS (Grillot and Guintini).

The valency of copper as an emission centre. The absence of electron spin resonance for ZnS(Cu) phosphors and moreover the measurement of magnetic susceptibility as a function of temperature show that the emission centre is due to Cu^+ ions. For neutral copper atoms ($Z = 29$) an odd number of electrons is present and cancellation of all spins is impossible, that is, the atom is paramagnetic. The same applies to Cu^{2+}, but in contrast Cu^+ is diamagnetic. Experiment shows

Fig. V.4 *Magnetic susceptibility* χ *of ZnS* $(9.10^{-5}\ Cu)$ *as a function of temperature T*

(Bowers & Melamed)

(Fig. V.4) that the susceptibility of ZnS(Cu) is sensibly independent of temperature (Bowers and Melamed).

A notable experiment due to Prener and Williams shows also that, no matter how it is introduced into the lattice, copper does not by itself form a luminescence centre. They prepared ZnS by acting on a zinc salt with hydrogen sulphide, the zinc salt being made from zinc previously irradiated with neutrons to produce the reaction:

$$Zn^{64}(n,\gamma) \longrightarrow Zn^{65} \longrightarrow {}^{65}Cu \text{ (by } K \text{ electron capture with half-life of 250 days)}$$
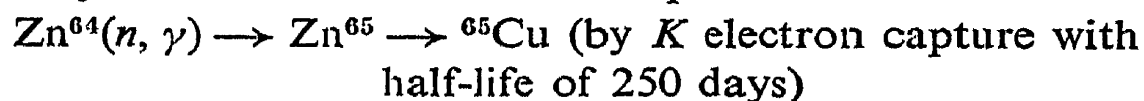
† The separation is the same for blende as for wurtzite, the small spectral shifts observed being attributable to the change in the width of the forbidden energy band.

Some copper is formed in this way inside the sulphide after firing. However, the emission bands are unaltered by its presence and so we conclude it is not the activator for these bands. There is some doubt about explanations of these effects. The copper may not be at a suitable site in the crystal lattice (i.e. not associated with a donor centre according to Williams), or perhaps, following an ionic model $Zn^{2+}S^{2-}$, it occurs as Cu^{2+} and not Cu^+ (Klick and Schulman).

Whatever the nature of the binding assumed for ZnS, most workers agree that copper introduces new levels situated several tenths of an electron volt above the top of the valence band. Using the purely ionic model (Klasens), the replacement of Zn^{2+} by Cu^+ reduces the bond strengths to the surrounding sulphur ions and increases the electrostatic energy for the electrons on these ions. This produces bands at a height e^2/Kd above the valence band (K is dielectric constant of the sulphide and d the nearest neighbour distances in the lattice). If on the other hand a purely covalent binding is assumed (Williams), then replacement of Zn ($Z = 30$) by Cu ($Z = 29$) allows only three of the four tetrahedrally direct covalent bands to be completed around the copper. This gives rise to an acceptor level which according to the Bethe model will be at an energy $13 \cdot 5$ eV$/K^2$ above the valence band. The similar conclusion for both the above approaches is thus probably a valid one. Detailed investigations consider the occupancy of the centre, the role played by the 'flux' in preparation and the difference between 'blue' and 'green' emission centres.

From the work of E. Grillot it would appear that introduction of oxygen produces the green emission centres. A halogen replacing sulphur (introduced by the flux during firing) will do the same (F. E. Williams). The centre can therefore be represented to a first approximation by a partially covalent 'molecule' formed by copper, the surrounding sulphur atoms and those of oxygen or a halogen associated with the group (with the exception of fluorine, which because of its high electronegativity does not favour covalent bonding).

Some discussion on recent models for luminescence centres in ZnS(Cu). A simple picture of the association between the copper ion and the halogen ion is given by Williams and Prener's model of *associated donor-acceptor centres* (see below, Fig. V.9). This kind of association requires that approximately equal concentrations of the activator and of the halogen (coactivator) have been deliberately introduced into the sulphide. For such experimental conditions the intensity of the

green band is much higher than the intensity of the blue band (see van Gool and Cleiren, 1960): this supports the assumption that the green band is due to the associated donor-acceptor system.

On the other hand, an excess of copper gives the blue copper fluorescence. This fact leads to the assumption that the blue band is *not* due to an association between the activator and the halogen ions (see, however, Kröger and Helligman, 1948).

The peak position of both bands is unaffected (within experimental limits) by the chemical nature of the halogen ion, for instance, Cl or I: the halogen effect is due to its substitutional charge $-e$ in the lattice.

Kröger and Dikhoff (1950) have shown that the trivalent elements Al, Ga, In may be used as coactivator ions instead of the halogens. The mechanism of the coactivation is probably approximately the same. However, they seem to introduce donor levels with depths slightly larger than the halogens (by 0·04 to 0·08 eV) and a displacement of the emission towards longer wavelengths is observed. When such an accuracy is possible many contradictions appear between the experimental results reported by different workers.

The numerous experiments performed by E. and M. Grillot have given evidence for the fact that oxygen ions may behave qualitatively in the same way as the above coactivators. It is quite certain that the incorporation of oxygen leads to donor levels in many semiconductors, and the same occurs probably in zinc sulphide. Indeed, the part played by oxygen in the improvement of electroluminescent phosphors also supports this assumption (see page 255). When neither halogen nor Al, Ga or In is present, the green emission is favoured by rather small concentrations of copper and the blue one by large concentrations; the limit depends on the amount of oxygen present in the sulphide. This behaviour is the same as that reported above for coactivated phosphors.

The following level scheme summarizes the above discussion. We must emphasize that many further experiments are needed for supporting or for abandoning it, but we think that it may be a good first approximation.

It is proposed that the same ground state, due to Cu^+ ions, plays its part in both blue and green centres in zinc sulphide. But the green emission occurs from a transition arising from the donor level introduced by the oxygen or the coactivator ions; the blue emission is

E

produced, either in a transition directly from the conduction band or in a transition from an excited level of the centre; this excited level must be shallower than the donor level involved in the green emission (Fig. V.5). van Gool (1961) suggests that an association with lattice defects is responsible for the blue emission.
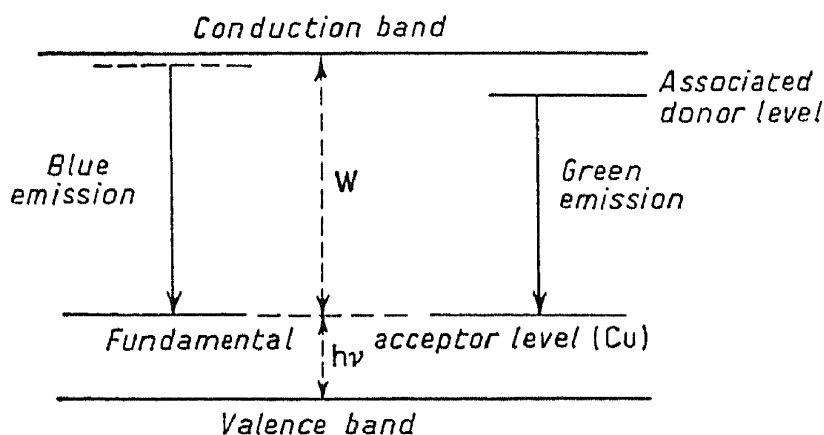
Fig. V.5 *A model recently proposed for blue and green emission centres in ZnS(Cu)* *(G. Curie and D. Curie)*
W is the energy necessary for exciting the centre in electroluminescence
hν is the energy involved in the infra-red quenching

The assumption that the same ground state occurs for both emission bands is supported by the following evidence:

(*A*) In electroluminescent cells using ZnS(Cu), no change of colour is produced when higher voltages are applied (Fig. IX.5); this behaviour is opposite to that of phosphors containing different activators. Thus the energy *W* for exciting blue and green centres is about the same.

On the contrary, the classical level scheme (Fig. V.3) suggests that the blue band grows in intensity with voltage faster than the green band, and this conclusion is not supported by experimental evidence.

(*B*) The same energy *hν* occurs in the infra-red quenching of both emission bands (Fig. VII.13). Garlick and Browne have shown that the infra-red quenching spectra are identical with the excitation bands.

On the other hand, the classical Riehl–Schön–Klasens scheme explains more easily the difference of temperature quenching between the blue and green emissions: the blue emission disappears at a temperature 100° to 150° lower than for the green one. However, this may also be explained with Fig. V.5 by using a remark due to

Roberts and Williams (1950): quenching occurs when the thermal activation of an electron from the excited level of the centres freeing it into the conduction band occurs before the light-emission transition. This activation is produced at lower temperatures for the blue centres.

In addition, the Cu level is split by the asymmetry of the electric field in the crystal (J. L. Birman). In our opinion, this splitting is probably not very much larger than the splitting of the valence band levels, i.e. some 10^{-2} eV. If this is true, it is much smaller than the widths of the emission bands.

2. Silver and gold as activators

While the copper activator is close to zinc in the periodic table, silver and gold are the higher 'homologues' of copper. The activation process is probably analogous, i.e. substitution of the metal in a zinc site and formation of a partially covalent molecule. The following table gives the location of the two main emission bands for zinc and cadmium sulphides.

TABLE V.5

	Type 'I' Centres	Type 'II' Centres
Cu in ZnS (wurtzite)	5,230 Å	4,450 Å
Cu in ZnS (blende)	5,350 Å	4,600 Å
Ag in ZnS (wurtzite)	4,760 Å	4,370 Å
Ag in ZnS (blende)	4,960 Å	4,500 Å
Au in ZnS (wurtzite)	5,300 Å	4,700 Å
Au in ZnS (blende)	5,500 Å	4,800 Å
Cu in CdS (wurtzite)	10,200 Å	8,200 Å
Ag in CdS (,,)	7,800 Å	7,160 Å
Au in CdS (,,)	11,500 Å	8,000 Å

Most of the emission bands of CdS are in the infra-red. In the case of CdS(Ag), centres of type II always give a red emission, but to obtain high emission efficiency firing must be made at the rather low temperature of 600°–800°C (E. Grillot).

In addition, the incorporation of a large amount of silver into cadmium sulphide produces a visible red emission, peaked at 6,200 Å (Fonda). We agree with a suggestion from van Gool, ascribing this emission to centres described by the model of Lambe and Klick (see Fig. V.9). The homologous band in ZnS is likely to be situated in the ultra-violet region (near 3,900 Å).

In several respects the behaviour of silver-activated samples

appears to be slightly different from that of Cu- and Au-activated zinc sulphide phosphors. The reason for these differences is not well understood. Until quite recent work, the long-wave band (type 'I' centres) of silver-activated ZnS was not observed. Henderson, Ranby and Halstead have given evidence for the occurrence of this band,
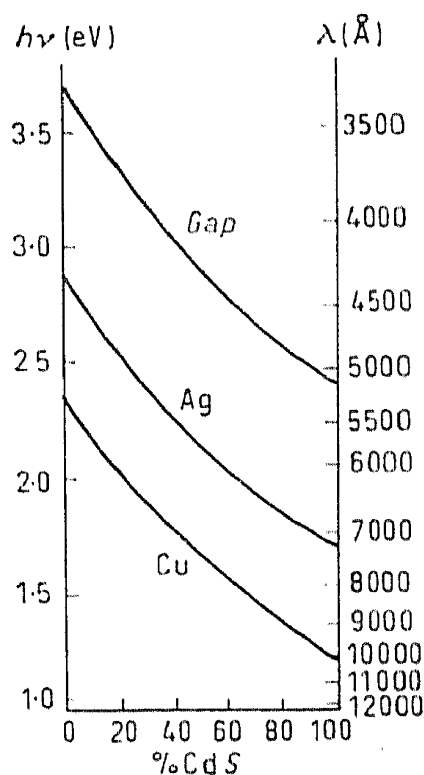
Fig. V.6 *Position of emission peaks as a function of composition for zinc–cadmium sulphides at room temperature. Molecular percentages of CdS*

Gap = *band gap*
Cu = *green band due to copper*
Ag = *main band of silver (blue emission)*

but its intensity remains small compared to the main blue-violet band (type 'II' centres). It is relatively enhanced at temperatures above room temperature: in this way, H. Payen de la Garanderie, of the author's laboratory, has confirmed the results of Henderson and co-workers, and shown that it is indeed the homologous band of the 7,800-Å band of CdS.

3. Radiative recombination due to vacancies (Kröger)

'Unactivated' or rather 'self-activated' zinc sulphide shows a blue emission. When it does not arise from unsuspected traces of copper†

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† Traces (~ 10^{-8} pts per ZnS) of Cu, Ag, &c., can be detected by radiochemical analysis: E. GRILLOT, *Congrès Soc. Sav.* (1955), p. 71.

is often attributed to zinc vacancies. At room temperature the emission peaks at 4,520 Å (Kröger and Dikhoff)[†] and is very close to the peak for copper and even for silver activators. We therefore ask if they do not arise from the same process in each case. However, Larach and Schrader have shown that the maximum for the blue emission of self-activated ZnS moves to longer wavelengths as the temperature is lowered (4,560 Å at 90°K), while the blue emission due to copper is shifted in the opposite direction (4,380 Å at 90°K). When impurity activator concentrations exceed 10^{-6} or 10^{-5} parts per ZnS or CdS, the emission attributed to vacancies disappears in favour of that due to the impurities.

In CdS the metal vacancy emission is peaked near 7,600 Å; thus, exactly in the same way as in ZnS, confusion is possible with the silver-activated emission.

In addition, a connection has been sometimes proposed between the sulphur vacancies and other emission bands.

Melamed ascribes the visible red emission of CdS(Ag) (6,200 Å), activated by an excess of silver, to the sulphur vacancies. *A priori*, this emission can also be ascribed to interstitial Ag^+ ions, or to pairs of Ag^+ ions: in the near future, polarization experiments will give the possibility of distinguishing between these different models.

We should remember that the analogous emission in ZnS occurs at 3,900 Å.

The sulphur vacancies have also been suggested as playing a part in the emission at 6,700 Å of ZnS(Cu) with an excess of copper (Froelich). This emission is commonly referred to as the 'red' emission (because the maximum of the emitted energy is in the red part of the spectrum) or as 'orange-red' (because the word describes the colour of the emission as observed). The possible models for the corresponding centres have been recently reviewed and discussed by Aven and Potter (1958). Pairs of copper ions are involved in these centres, but they may be associated with a sulphur vacancy.

4. Manganese (Mn^{2+}) as an activator

As an activator in ZnS phosphors manganese gives a characteristic yellow-orange emission. Its behaviour is different from those due to Cu, Ag and Au activators. Although photoconduction can be

[†] This figure is for wurtzite ZnS. In blende (Lewchin, 1961) the peak is situated at 4,690 Å.

excited in ZnS(Mn), particularly if 3,650 Å radiation is used, the Mn^{2+} ion produces a series of discrete absorption bands (see Fig. V.7), and by irradiation in one of these bands (e.g. with 4,358 Å Hg line)
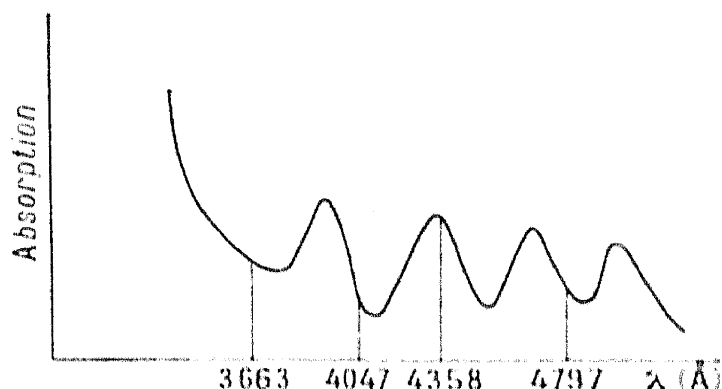
Fig. V.7 *Absorption spectrum of a ZnS–MnS (2 per cent) phosphor (F. A. Kröger)*

a fluorescence unaccompanied by photoconduction or phosphorescence of long duration is produced, the decay being sensibly independent of temperature. The emission is due to transitions within the Mn^{2+} ion, the main transition being due to a change in spin of one of the five $3d$ electrons (see Fig. V.8).

The stable configuration of a neutral manganese atom is as follows:

$$Mn \quad 1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^2 \quad 3p^6 \quad 3d^5 \quad 4s^2$$
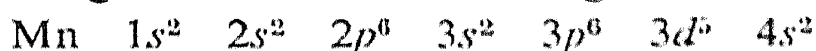
The energy-level system for the free manganese ion Mn^{2+} ($1s^2 \ldots 3d^5$) gives the spherically symmetrical ^6S state as the ground state, in which all $3d$ electron spins are parallel, while the first excited state is ^4G having one of the spins reversed. The series of levels for the ion is as follows:

$$^6S, \quad ^4G, \quad ^4P, \quad ^4D, \quad ^4F$$
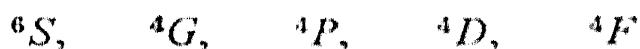
The energy separation between the ground and the first excited state is 3·32 eV. The excited state ^4P is only a little higher. The excited state $3d^44s$ is some 7·2 eV above the ground state and, as Kröger assumed, it cannot be involved in the observed emission. Johnson and Williams have determined the magnetic dipole moment for Mn^{2+} in the ground and in the excited states for the ion in a ZnF_2 lattice, and have found that it is much weaker by about one Bohr magneton in the excited state, which indicates a lower multiplicity in the excited state (probably ^4G).

Fig. V.8 *The transition* $^4G \longleftrightarrow {}^6S$ *in the* Mn^{2+} *ion*

The crystal field splitting for the ground state ^6S is extremely small $\approx 10^{-3}$ cm^{-1}. This splitting is larger for the excited state ^4G; but theoretical calculations, which have been made by different authors (Tanabe and Sugano, Clogston, &c.) lead to the conclusion that it remains small enough to describe the emitting level as arising from the ^4G state of the free ion.

The emission due to Mn^{2+} ions is often in the yellow-orange region, as is the case for ZnS–Mn and ZnF_2–Mn. However, a notable exception is willemite Zn_2SiO_4–Mn, where the emission is green (the same is true of CaF_2–Mn).† These differences are attributed to a different interaction between the Mn^{2+} ion and the surrounding lattice which can be described by a configuration coordinate scheme as for Tl^+ ions in KCl. Only in the case of willemite has this been done (Klick and Schulman, Vlam – see Chapter III.1).

TABLE V.6

Emission peaks for the Mn^{2+} ion luminescence

Mn^{2+} free ion	3,730 Å
Mn^{2+} in ZnS	5,850 Å
Mn^{2+} in ZnF	5,950 Å
Mn^{2+} in Zn_2SiO_4	5,200 Å

The transition due to spin reversal is normally forbidden. The spin-orbit coupling makes it possible to have a mixture of ^6S and ^4P states (Leverenz) and the probability of such a transition is strongly dependent on lattice interaction; the more the binding is covalent the more probable it becomes.

TABLE V.7

Excited state life times for Mn^{2+} centres

Mn^{2+} in ZnF_2	0·1 sec
Mn^{2+} in Zn_2SiO_4	0·013 sec
Mn^{2+} in ZnS	0·0004 sec

Phosphors activated by Mn^{2+} ions provide ideal subjects for electron spin resonance studies (Kastler, Hershberger, Uebersfeld, &c.).

† The manganese emission is also orange or yellow in halophosphates phosphors (see page 62), in calcium and cadmium silicates (Fonda), &c. However, since the free ion transition would be, if observed, in the ultra-violet part of the spectrum, all colours are theoretically possible for Mn^{2+} embedded into different crystals. A red emission is found with $Zn_3(PO_4)_2$–Mn; a search for a blue emission has been made by E. Lind for CaF_2+BeF_2(Mn) phosphors.

An applied magnetic field H splits each energy level by a Zeeman effect into $2J+1$ components with spacings

$$\Delta E = g\frac{eh}{4\pi mc}\mathscr{H}$$

while a high-frequency field (frequency ν) is applied in a perpendicular direction to $\mathscr{H}$. The transition probability between two adjacent levels is a maximum when $\mathscr{H}$ is of such a magnitude to give a resonance

$$h\nu = \Delta E$$

For the ground state ($J = 5/2$), five transitions can occur, but the same applies to each at resonance.

Hershberger and Leifer have examined thirty-two phosphors activated by manganese. They first looked at the electron resonance absorption for the unexcited phosphors and their results confirm the assumed symmetry of the ground state (i.e. ^6S) with an isotropic g value of about 2. However, a marked hyperfine structure sometimes occurs.

Since the nuclear spin of manganese is $I = 5/2$, a hyperfine spectrum with six components occurs. This is found for dilute aqueous solutions containing Mn^{2+} ions (Kip) and also for ZnS(Mn) (blende form). This structure is easily explained using the Hamiltonian

$$H_{Mn^{2+}} = g\frac{eh}{4\pi mc}\mathscr{H} + A\mathbf{S}.\mathbf{I}$$

involving coupling between nuclear spin $\mathbf{I}$ and electron spin $\mathbf{S}$. If M is the electronic magnetic quantum number and m that for the nucleus, then we have the selection rules

$$\Delta M = 1; \qquad \Delta m = 0$$

from which we have six absorption lines corresponding to the $2I+1 = 6$ values of m.

For hexagonal ZnS, thirty lines have been observed, and this has been explained by a theory due to Abragam and Pryce which assumes an asymmetric electric field around the Mn^{2+} (perhaps due to a vacancy). This produces a correction of an axial and non-spherical kind to the Hamiltonian of the form

$$H_{Mn^{2+}} = \text{expression above} + D[S_z^2 - \tfrac{1}{3}S(S+1)]$$

The selection rule $\Delta M = 1$ thus allows five series of lines for each of the six hyperfine structure lines (i.e. for each of the m values). Thus Hershberger was able to account for the thirty lines observed.

The change in the electron resonance spectra when the phosphor is excited has also been investigated. A. Kastler had already shown the interest which existed in applying the resonance technique for the excited state. However, since Hershberger used 3,650 or 2,537 Å radiation which produces photoconductivity, even in ZnS(Mn), and not radiation lying in a characteristic absorption band of the manganese, large effects due to the conduction electron absorption occur (even without the applied magnetic field). These mask the spin resonance effects (which of course occur only at certain magnetic field values).

III. OPTICAL TRANSITIONS INVOLVING LOCALIZED LEVELS

1. Luminescence centres and electron traps in a photoconducting crystal phosphor

Let us first recall the definitions given in the introduction:

(i) Luminescence centres are the energy levels responsible for the spectrum of the emitted luminescence.

(ii) Electron traps are metastable levels responsible for phosphorescence after excitation has finished.

In an atom or in a luminescent crystal such as KCl(Tl), where the emitter system is 'quasi-atomic' (Tl^+ to a first approximation), it is easy to know whether or not a metastable state is involved. Thus the levels $^1P_1$ and $^3P_1$ of the thallium are emission levels with short life times, but $^3P_0$ constitutes an electron trap because the J value is zero as for the ground state $^1S_0$.

In a photoconducting crystal such as ZnS(Cu), both the centres and traps are localized levels in the forbidden energy gap and can capture free electrons and free positive holes. The distinction between them is no longer so clearly marked and depends on their relative capture cross-sections for the two different types of carriers, σ_e for conduction electrons and σ_h for positive holes in the valence band. We obtain a recombination centre for electrons and holes if a level has $\sigma_e \approx \sigma_h$ and an electron trap if $\sigma_e \gg \sigma_h$.† So far it has always been possible to say for the given conditions whether a given level will behave as a trap or a recombination centre. However, the behaviour is very dependent on experimental conditions. Thus copper

† For traps in CdS the ratio of the capture cross-sections for the two types of carrier is of the order of 100,000 (R. H. Bube).

in germanium gives three acceptor levels (accepting 1, 2 or 3 electrons to complete the tetrahedral covalent bonding around the copper) situated at 0·04 eV and 0·32 eV above the valence band and at 0·26 eV below the conduction band (Woodbury and Tyler). The level at 0·32 eV behaves as a recombination centre in N-type germanium at room temperature. However, while the capture cross-section for holes is almost independent of temperature, that for the electrons σ_e depends on a thermal activation with energy 0·2 eV (this activation is necessary to obtain the configuration in which the capture transition is most likely). At liquid air temperature, therefore, this level becomes a positive hole trap. Such effects have not been found for ZnS: however, Arpiarian and also Gergely have shown that in ZnS(Au+Ni, Co or Fe) the respective capture probabilities for the centres Fe, Ni and Co (with or without radiative emission), i.e. their functioning as 'killer' centres or luminescence centres, depends on the temperature and also on their concentrations. This behaviour is, however, rather exceptional.

In general, as shown by Fig. 5 of the Introduction, a level which is normally empty and lying near to the conduction band behaves as an electron trap, while a level normally occupied and near to the valence band behaves as a positive hole trap. A level approximately midway between the bands acts as a radiative or non-radiative recombination centre. This can be demonstrated by the following qualitative argument which is from P. Aigrain:

Suppose that the matrix element representing the capture probability for a conduction electron by a localized level is given by

$$\phi_k = v_k \exp(i\mathbf{k}.\mathbf{r})$$

This can be written

$$\int \psi(r)\frac{e}{mc}\frac{\hbar}{i}(\mathbf{A}.\mathbf{grad})\psi_k \, d\tau$$

$\psi(r)$ can be resolved into a series of Bloch functions of the type

$$\psi(r) = \sum_{k'} A_{k'}v_{k'} \exp(i\mathbf{k'}.\mathbf{r})$$

As in Chapter IV, the term $A_{k'}$ only gives an appreciable matrix element for $k' = k$. This means that the transition probability is only large when the coefficient $A_{k'}$ is large.

During phosphorescence the conduction electrons diffuse to the bottom of the conduction band for which we assume $k = 0$. The

radiative capture of these electrons by the level $\psi(r)$ will have a probability of the form

$$P_{\text{capture}} \propto |A_{k=0}|^2$$

which is large if $A_{k=0}$ is large.

For a trap near to the conduction band the coefficient $A_{k=0}$ for the bottom of the band will generally be large while the contributions of the Bloch functions to the valence band will be small, which gives a high probability for conduction electron capture and a low probability for the electron to fall into one of the holes in the valence band. For a deeper level the large A_k values correspond to energies $\mathscr{E}(k)$ situated higher up in the band (as far above its bottom as the localized level is below). However, if the level is sufficiently localized and its Fourier transform sufficiently extended, the coefficients $A_{k\sim 0}$ can have sufficient amplitudes to allow capture with a significant probability. If, however, the level is too deep and its Fourier transform not extensive, then $A_{k=0}$ will be negligible and that will also apply to the capture probability.

Quantitative calculation of the radiative capture probability has been made by Parodi for a hydrogenlike level. Capture in such a level appears to lead to observable transitions in germanium and certainly in silicon.

2. Various types of centres in photoconducting phosphors

Three types of model can be assumed for the centres in a photoconducting phosphor:

(*a*) *Centres near to the conduction band.* These centres are simply deeper than typical electron traps, and transitions to the valence band although less probable than those from the conduction band to these centres still have an appreciable probability. This model was postulated for CdS by Lambe and Klick and for certain bands of ZnS(Cu, Sm) by V. V. Antonov-Romanovsky. First of all, a conduction electron is captured in the localized level and then this electron falls into a hole in the conduction band, this last and radiative transition giving emission. Most workers consider that special conditions must apply for such transitions to occur. This really arises from the intuitive feeling that the very low positive hole mobility in phosphorescent sulphides mitigates against them (the 'macroscopic' hole mobility in CdS is $\approx 10^{-4}$ while that of the electrons lies between 10 and 100 cm^2/volt sec).

According to Schön the centres responsible for the Ewles–Kröger emission (Chapter IV, paragraph II.2) are of this type.

(*b*) *Centres near to the valence band.* This is the 'classical' model for copper centres in zinc sulphide (Riehl–Schön–Klasens). Copper produces a level in the forbidden energy band several tenths of an electron volt above the valence band which has a high probability for positive hole capture (it is assumed that a hole diffusing through the valence band is immediately captured by the centre when it lies below it in the band diagram). The centre also is allowed a significant capture probability for conduction electrons, and this gives rise to luminescence as observed by a transition to the centre ground state from the bottom of the conduction band. Fig. V.3 was drawn on the basis of this model.

(*c*) *Centres involving a ground state* (*I*) *near the valence band and an excited state* (*II*) *near to the conduction band.* After the discussions given earlier we can see that the levels I have a high hole capture probability and levels II a high electron capture probability. After capture has taken place in each type, emission can take place by a transition of the electron from level I to level II. The only condition is that the temperature is not too high, so that electrons are not freed by activation from the type II levels before the transition can take place. We can affirm that if such centres exist, *the probability of radiative capture will be higher than for the other types of centres considered in the two models of* (*a*) *and* (*b*) *above.*

Williams and Prener suggested the following idea:

Copper with nuclear charge $Z = 29$, one less than zinc with $Z = 30$, produces, as already seen, a level just above the valence band. The coactivator chlorine with $Z = 17$, one more than sulphur with $Z = 16$, introduces a 'donor' level just below the conduction band. These levels are equivalent to those denoted by I and II respectively above, and they arise from a centre produced by copper in association with chlorine. The association arises simply from the electrostatic attraction between the two impurities. This idea assumes a halide flux to have been used in preparation of the sulphide. This model was discussed on page 116 for zinc sulphide.

The transition probability will be very sensitive to the amount of overlap between the levels I and II and is essentially determined by the covalent character of the binding. The quantitative calculation is very complex and has not yet been completed.

Polarization of the fluorescence emission of impurity-activated phosphors. The emission from cubic zinc sulphide crystals is not polarized, even if polarized radiation is used for excitation, but the emission from hexagonal ZnS and CdS single crystals, activated by Cu, Ag, Au, is polarized preferentially with E perpendicular to the optical z-axis (Birman and Lempicki).

This result can be explained with any of the above models if we assume that a level situated near the valence or the conduction band
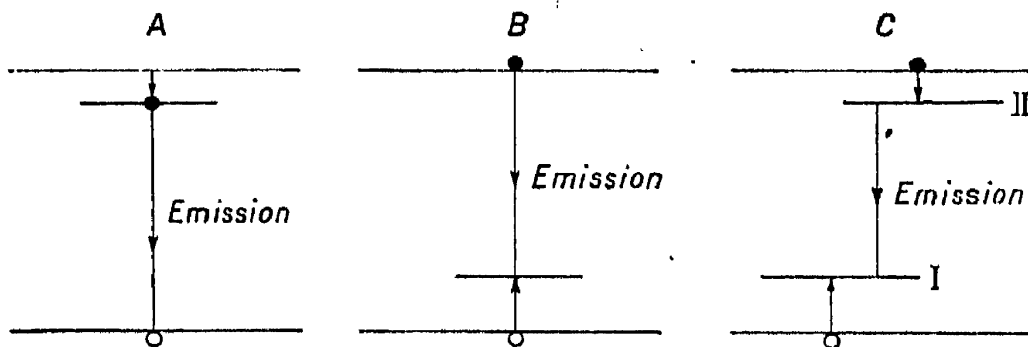
Fig. V.9 *Various centre models*

A *The Lambe and Klick model; emission occurs when a captured electron recombines with a hole in the valence band*

B *'Classical' model of Riehl, Schön and Klasens; emission occurs when a conduction electron is captured by an empty centre*

C *Associated donor-acceptor centre; hole capture in the ground state I and electron capture in the excited state II is followed by transition of the electron from II to I giving emission (Williams–Prener model)*

has the same symmetry as the neighbouring band. It seems that this hypothesis is valid, at least as an approximation. More elaborate computations, taking into account the differences between the symmetry of a shallow localized level and the neighbouring band, are necessary in order to use polarization experiments for choosing between the three models of Fig. V.9.

Sometimes, dichroism effects appear (the radiation with $E \perp z$ is more strongly absorbed in the crystal than the radiation with $E \parallel z$) and conceals the above effects (Keller and Pettit).

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Electron Traps, Phosphorescence, Thermoluminescence

I. DEFINITION OF TRAPS – MEAN LIFE TIMES – EFFECTIVE CROSS-SECTIONS

1. Definitions

Electron traps are metastable states or levels in which electrons can be captured and remain for significant times between excitation (absorption of exciting radiation) and emission of luminescence. They are the levels responsible for the persistence of phosphorescence while the centres are the levels which determine the luminescence spectra (cf. Introduction and Chapter V, §III).

An electron raised into an excited state (i.e. into the conduction band in the case of a photoconducting phosphor) can

(a) recombine with its original centre giving fluorescence emission;

(b) fall into a trap; it will escape after a mean life time τ and can then recombine with an empty centre giving phosphorescence emission at a time τ after the original excitation.

The electron freed from a trap may, alternatively, be retrapped, and in this case the ultimate phosphorescence will be delayed. The thermal activation energy E required to liberate a trapped electron is known as the trap depth, the energy being received by phonon interaction with the surroundings. If p is the probability of liberating the trapped electron per second, then $\tau = 1/p$ and

$$p = s\,e^{-E/kT}$$

$$\log_e \tau = \frac{E}{kT} - \log s$$

We give some typical numerical values of τ for various trap depths assuming $s = 10^9/\text{sec}$ and $T = 18°C$:

TABLE VI.1

τ	E
1 sec	0·52 eV
1 min	0·62 eV
1 hour	0·725 eV
1 day	0·805 eV

Traps responsible for phosphorescence observed at room temperature for such an s value have thus depths between 0·5 and 0·8 eV.

The mean life at various temperatures for $S = 10^9/\text{sec}$ and $E = 0·65$ eV (an important case in ZnS(Cu) where such traps cause the room temperature phosphorescence of the order of minutes) is as follows:

TABLE VI.2

T	$-100°C$	$-50°C$	$18°C$	$50°C$	$100°C$	$150°C$
τ	1,600 days	1 day	3 min	4 sec	0·25 sec	0·03 sec

Thus a trap important in phosphorescence at ordinary temperatures is not so at temperatures 100°C away on each side (Lewchin).

2. Thermal activation of trapped electrons

The above exponential expression for τ, with s a constant, is well supported by experiment. There are not many direct verifications
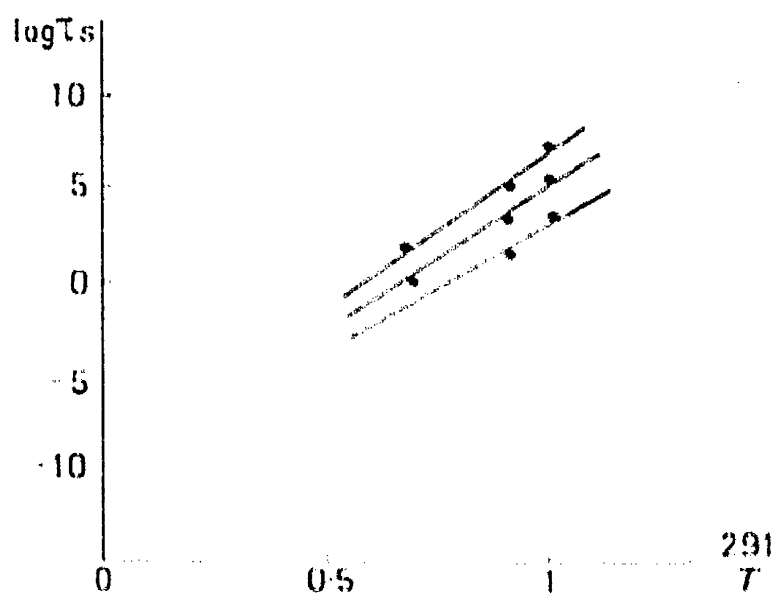

Fig. VI.1 *Variation of the life times of three groups of traps in CaS(Bi) with temperature*

available such as those given by the curves of Fig. VI.1, but thermo-luminescence-curve theory constantly uses this expression as a basis and this leads to no contradictions.

For a given trap depth E, s does not appear to vary much with temperature T, at least it does not affect the linearity of the $\log \tau$ vs. $1/T$ graphs (a proportionality between s and T would not affect the linearity). We can therefore usually assume $s(T)$ is a constant in the interpretation of experimental results.

However, even in the same phosphor s does not necessarily have the same value for traps of different depths. Such variations in s with E have not been very much studied. Only s values of about 10^8 to 10^9/sec have been used for different groups of traps as, for example, those due to copper in zinc sulphide. In germanium and silicon, higher values of s of the order of 10^{11} to 10^{14}/sec have been indicated (Haynes, M. Lax), but there are few systematic studies available.

Different workers have envisaged different processes for the escape of trapped electrons. However, as soon as a thermal activation is assumed, all the different theories must involve a Boltzmann factor in the probability p.

We give now a semi-classical approach to the problem of activation of trapped electrons.

Consider a trapping model with levels equidistant in energy from each other, the spacing being $h\nu_c$ (i.e. oscillators of characteristic frequency ν_c). By successive absorption of phonons of energy $h\nu_c$ the trap system reaches higher and higher excited levels, that is, th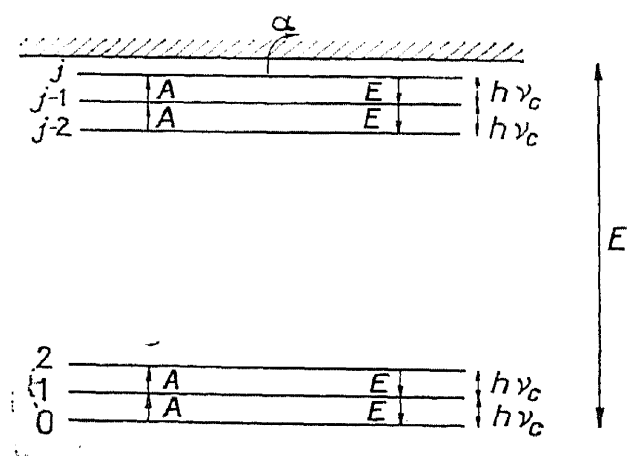e surrounding ions have increasing vibrational energies. When the trap is in a certain state $jh\nu_c$ the electron will be freed (Fig. VI.2).

The absorption probability for a transition kth $\longrightarrow$ $(k+1)$th level

Fig. VI.2 *Progressive excitation of an electron trap*†

† An analogous calculation for a chemical reaction requiring a similar activation of molecules has been given by NIKITINE, E. E. (1957) 'On deviations from the Boltzmann distributions in the dissociation of diatomic molecules', *Dokl. Akad. Nauk S.S.S.R.*, **116**, 584.

will be proportional to the number of phonons of frequency $h\nu_c$:

$$A = a\frac{1}{(e^{h\nu_c/kT}-1)}$$

The emission probability (return from $(k+1)$ to k) will be

$$R = a\left(1+\frac{1}{(e^{h\nu_c/kT}-1)}\right)$$

We thus obtain a set of differential equations:

$$\begin{cases}\dfrac{dn_0}{dt} = \qquad\quad -A \qquad\quad n_0 + R \quad n_1 \\[2mm] \dfrac{dn_1}{dt_t} = An_0 \quad -(A+R) \quad\;\; n_1 + R \quad n_2 \\[2mm] \cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot \\[2mm] \dfrac{dn_{(j-1)}}{dt} = An_{j-2}-(A+R) \quad n_{j-1}+R \quad n_j\end{cases}$$

where n_k is the number of traps in the state k.

If the system extends to $k = \infty$, then there is an equilibrium solution

$$n_0 = \text{const.}, \qquad n_j = n_0\, e^{-jh\nu_c/kT}$$

and the occurrence of the Boltzmann factor in the probability p is easily explained: it is given by the Boltzmann factor and is the number of traps in the state j.

However, this elementary approach is incorrect since the traps are emptied as soon as they reach the jth state, which causes a perturbation of the Boltzmann distribution. The set of equations must be modified thus:

$$\left\{\frac{dn_j}{dt} = An_{j-1}-(\alpha+R)n_j\right\}$$

where α is the probability of the transition of the trapped electron from the jth state into the conduction band.

Between the n_k traps in the kth state an equilibrium will be established in which they decay exponentially with time:

$$n_k = \chi_k\, e^{-pt}$$

p being the smallest root of the characteristic determinant of the modified set of differential equations. We thus have

$$p = \alpha\,\frac{(e^{h\nu_c/kT}-1)^2}{e^{h\nu_c/kT}+\dfrac{\alpha}{A}-1}\; e^{-(j+1)h\nu_c/kT}$$

which is obviously of the form

$$p = s\, e^{-E/kT} \quad\text{where}\quad E = (j+1)h\nu_c$$

3. Thermodynamic expression of Williams and Eyring (The 'Absolute Rate Theory')

For constant volume the free energy F of a system (given by $F = U - TS$ with the usual notation) plays the role of the thermodynamic potential. It follows that the rate of a chemical reaction, here the escape of trapped electrons and a monomolecular reaction, depends on a thermal activation which will depend on the variation ΔF in the free energy according to a Boltzmann factor

$$p = K e^{-\Delta F/kT} = K e^{\Delta S/k} \cdot e^{-\Delta U/kT}$$

where ΔU is the activation energy and ΔS the activation entropy.

The coefficient K has the form $x\nu_t$, and so $p = x\nu_t e^{\Delta S/k} e^{-\Delta U/kT}$, the factor $e^{\Delta S/k}$ (assuming $S = k \log W$) being the probability that the system, having obtained the necessary activation energy, will reach the configuration from which the electron is freed; ν_t is the thermal vibration frequency for this configuration and x is a 'transmission coefficient'. These various factors are all lumped together in the constant s, ν_t is of the order of 10^{12} to 10^{13}/sec, not necessarily of the same order as s, to which we sometimes wrongly give the name 'escape frequency' since only ν_t merits that name. When s is markedly less than ν_t, χ is small and $\Delta S < 0$.

4. Relation between the escape probability p and the effective capture cross-section σ of the trap

This relation, due to Mott, is obtained by use of the law of detailed balancing.

Suppose there are n_0 traps per c.c of which n are empty and $n_0 - n$ occupied, and that there are n electrons in the conduction band with thermal velocity u where

$$u = \sqrt{\frac{3kT}{m}} \qquad (\tfrac{1}{2}mu^2 = \tfrac{3}{2}kT)$$

The number of electrons captured per second by each trap is given by $\sigma n u$ and the number captured per second by any of the n empty traps is

$$\sigma n^2 u = (n_0 - n)p$$

for equilibrium.

Now

$$\frac{n^2}{n_0 - n} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} e^{-E/kT}$$

But this ratio is also given from above by $\dfrac{p}{\sigma u}$ and so

$$\frac{p}{\sigma} = \frac{2\pi m (kT)^2}{h^3} \sqrt{6\pi} \, e^{-E/kT}$$

and if we assume $p = s \, e^{-E/kT}$ and σ to be a constant we have at ordinary temperatures the numerical relation

$$\frac{s}{\sigma} \approx 1 \cdot 5 \cdot 10^{26}$$

For copper-activated zinc sulphide, for which $s \approx 10^8$ to 10^9/sec, σ will lie between 10^{-18} and 10^{-17} cm².

For such cross-sections and for concentrations of conduction electrons $n \approx 10^{17}$/c.c, the mean free paths of electrons before capture will be given by

$$l = \frac{1}{\sigma n}$$

and can reach or exceed one centimetre. The experiments of Gudden and Pohl on the saturation of the primary photocurrent in zinc blende lead to paths of this order of magnitude.

In germanium, evidence has been given of values of s and σ that may be larger by more than three or four orders of magnitude than the above. For instance, the positive hole trap due to copper, operative at liquid air temperature (page 126), has a cross-section $\sigma \approx 10^{-13}$ cm² (Newman and Tyler); for the electron trap, due to Sb⁺, $\sigma \approx 10^{-12}$ cm² (Koenig). M. Lax has given to such traps with such large cross-sections the name of 'giant traps'. The corresponding values of the parameters are not very different from the frequencies of thermal vibrations and are perhaps even larger.

Such long paths are not actually found except when high electric fields are applied. The occurrence of thermal lattice vibrations (phonon interactions) and scattering and capture by impurity and lattice defects limit the mean free path far more than capture in traps. It is likely that the natural zinc blende crystals selected by Gudden and Pohl were more perfect than synthetic crystals currently available.

II. DECAY OF LUMINESCENCE

1. Monomolecular and bimolecular mechanisms

We usually distinguish two kinds of luminescence process, that with kinetics of the first order (monomolecular mechanism) and that having second-order kinetics (bimolecular mechanism).

It is generally accepted, but not quite correct, to use these terms, taken from chemical kinetics, as synonymous for such processes. A bimolecular reaction is one in which two molecules combine. In photoconducting luminescent solids there occurs in all cases a 'bimolecular recombination' of electrons and empty centres, but the kinetics may be of first or of second order, depending on the particular conditions. However, if this is generally understood, then the term bimolecular can still be applied to the particular case of a second-order kinetics recombination.

(*A*) *First-order kinetics.* The number of excited electrons n decreases according to a constant probability law

$$\frac{dn}{n} = -\alpha \, dt$$

which gives $n = n_0 \, e^{-\alpha t}$, and since the luminescence intensity $I = \dfrac{dn}{dt}$, then

$$I = I_0 \, e^{-\alpha t}$$

(*B*) *Second-order kinetics.* The probability for recombination is proportional to the number of available centres

$$\frac{dn}{n} = -\alpha n \, dt$$

and so n decreases hyperbolically with time

$$n = \frac{n_0}{(1 + n_0 \alpha t)}$$

the luminescence decay then being given by

$$I = \left| \frac{dn}{dt} \right| = \alpha n^2$$

thus $$I = \frac{I_0}{(1 + at)^2} \quad \text{where} \quad a = \sqrt{I_0 \alpha}$$

The decay thus becomes more rapid as the excitation intensity is increased.

Kinetics of fluorescence. The above kinetics can only apply to fluorescence (see definition in Introduction) since their foundation does not consider the intermediate process of trapping.

When luminescence is due only to transitions within the luminescence centres the monomolecular mechanism applies. If the optical transition is permitted (dipole), the mean life time in the excited state α^{-1} is of the order of 10^{-8} sec, the mean life time for transitions

in isolated atoms. However, we find forbidden transitions of much longer life time, for example for uranyl salts (10^{-4} to 10^{-3} sec), internal transition in Mn^{2+} ions (10^{-3} sec in ZnS, 10^{-2} in willemite, Zn_2SiO_4; cf. page 123).

In the case of the long duration fluorescence of the Mn^{2+}, which is more or less independent of temperature, this is often mixed with a short-period phosphorescence due to shallow electron traps and having a strong temperature dependence (Fonda).

However, even in this case of internal emission transitions the luminescence processes would really only be confined to the centre if a low-intensity excitation occurs in its characteristic absorption bands and if the crystal possesses no defects or impurity except the activator impurity. In actual practice the kinetics of fluorescence are sometimes more complicated (Louchtchik, Antonov-Romanovsky and co-workers). We have discussed above (see page 36) the phenomena occurring in KCl(Tl). In ZnS(Mn) the traps are not metastable levels of the Mn^{2+} ion (Lewchin and Tunitskaia): an excitation occurring in the characteristic bands of manganese (4,358 Å) produces a small photoconduction effect and thus these traps are hardly filled: on the contrary, excitation using 3,650 Å radiation involves a large photoconduction effect and marked filling of these traps occurs. In the same way, it is possible to find evidence for an electron-hole recombination in the uranyl salts (experiments by Lewchin, Gutan and Karzhavina, using cathode-ray excitation), while as a general rule (ultra-violet excitation) the case of uranyl salts gives one of the most characteristic examples of a simple exponential decay fluorescence.

In the case of sulphide phosphors of the ZnS(Cu) type, the short duration emission seems to involve first of all a monomolecular decay with a life time characteristic of transitions in isolated atoms, the transition occurring in emission centres (Kallmann),† and finally an approximately bimolecular decay with a life time of the order of 10^{-5} sec due to electrons, previously liberated, recombining with emission centres. All this is followed by a slower decay (10^{-4} to 10^{-2} sec) with complex kinetics and which is really a short-period phosphorescence due to traps of 0·3 or 0·4 eV in depth. Finally, there follows a long-period phosphorescence.

† See Chapter X, page 303; α-particle scintillations in zinc sulphide.

2. Kinetics of phosphorescence in photoconducting phosphors

To describe phosphorescence decay the preceding differential equations must be replaced by systems of differential equations containing several variables.

Let n be the number of trapped electrons and ν the number of conduction band electrons. The kinetics of phosphorescence depend on the spatial relations between luminescence centres and traps and on the motion of the conduction electrons.

Suppose two neighbouring centres are about 10^{-6} to 10^{-5} cm apart:

(*A*) If the traps are located near to the centres (less than 10^{-6} cm away) and only very small movement of electrons occurs from trap to centre, and vice versa, then we may consider each 'centre and neighbouring trap' as an independent unit giving a constant recombination constant with time. First-order kinetics then apply and traps of mean life time τ release electrons according to the relation

$$n = n_0\, e^{-t/\tau}$$

The short life time centre level is thus replenished by electrons from traps in a similar way to the case in radioactivity where a short-lived element (say radon) is formed by break-up of a long-lived element (radium). There is an equilibrium condition in which the activities of the two elements are equal, but their abundances very different (in the ratio of their life times).

In phosphorescence of this type the number $d\nu$ of electrons recombining with centres equals the number arriving from traps:

$$d\nu = dn$$

with the condition

$$\frac{\nu}{n} = \frac{\text{life time in conduction band}}{\text{life time in traps}} \ll 1$$

The luminescence intensity is given by

$$I = \frac{d\nu}{dt} = \frac{n_0}{\tau}\, e^{-t/\tau}$$

and an exponential decay law results. This is equally valid if instead of a conduction band we have an excited state of a centre, the trap being a metastable state. If a distribution of trap depths is present, $n_{0\tau}\, d\tau$ being the number filled initially with life times between τ and $\tau + d\tau$, then

$$I = \int_0^\infty \frac{n_{0\tau}}{\tau}\, e^{-t/\tau}\, d\tau \tag{1}$$

(*B*) If the traps are spatially independent of the centres and electron displacements are large enough for recombination with any of a large number of centres (i.e. $> 10^{-5}$ cm), the recombination probability is proportional to the number of empty centres and second-order kinetics apply.

Consider the case for traps of one mean life time (τ) only. Let n_0 be the total number of traps per c.c, n the number of filled traps and thus (n_0-n) the number of empty traps. Let ν be the number of conduction electrons and N the number of empty centres. If all centres are normally occupied and are emptied by excitation, then $N = n+\nu$.

We can then write

$$\frac{d\nu}{dt} = \frac{n}{\tau} - a_cN\nu - a_t(n_0-n)\nu$$

$$\frac{dn}{dt} = a_t(n_0-n)\nu - \frac{n}{\tau}$$

and
$$I = a_cN\nu$$

(a_c is the effective cross-section of centres multiplied by the thermal velocity of the electrons; a_t is the similar product for the empty traps).

We can obtain a rigorous analytical solution only when $a_c = a_t = a$, which corresponds to equilibrium between the conduction band and traps:

$$\frac{\nu}{n} = \frac{1}{an_0\tau}$$

($1/an_0$ is the effective life time for electrons in the conduction band). The two differential equations above give

$$\frac{dn}{dt} = -\frac{n^2}{n_0\tau}$$

which has the solutions

$$n = \frac{\tau n_0}{t+t_0}; \qquad \nu = \frac{1}{a(t+t_0)}$$

where t_0 is an integration constant equal to τ for saturation excitation, i.e. all traps filled at $t = 0$.

The luminescence intensity $I = a(n+\nu)\nu$ decays according to the simple law

$$I = \frac{\text{const.}}{(t+t_0)^2}$$

The equilibrium conditions are not necessarily valid throughout the decay, but are applicable after about 10^{-5} sec of decay.

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and an exponential decay law results. This is equally valid if instead of a conduction band we have an excited state of a centre, the trap being a metastable state. If a distribution of trap depths is present, $n_{0\tau} \, d\tau$ being the number filled initially with life times between τ and $\tau + d\tau$, then

$$I = \int_0^\infty \frac{n_{0\tau}}{\tau} \, e^{-t/\tau} \, d\tau \tag{1}$$

(*B*) If the traps are spatially independent of the centres and electron displacements are large enough for recombination with any of a large number of centres (i.e. $> 10^{-5}$ cm), the recombination probability is proportional to the number of empty centres and second-order kinetics apply.

Consider the case for traps of one mean life time (τ) only. Let n_0 be the total number of traps per c.c, n the number of filled traps and thus ($n_0 - n$) the number of empty traps. Let ν be the number of conduction electrons and N the number of empty centres. If all centres are normally occupied and are emptied by excitation, then $N = n + \nu$.

We can then write

$$\frac{\mathrm{d}\nu}{\mathrm{d}t} = \frac{n}{\tau} - a_c N\nu - a_t(n_0 - n)\nu$$

$$\frac{\mathrm{d}n}{\mathrm{d}t} = a_t(n_0 - n)\nu - \frac{n}{\tau}$$

and
$$I = a_c N\nu$$

(a_c is the effective cross-section of centres multiplied by the thermal velocity of the electrons; a_t is the similar product for the empty traps).

We can obtain a rigorous analytical solution only when $a_c = a_t = a$, which corresponds to equilibrium between the conduction band and traps:

$$\frac{\nu}{n} = \frac{1}{a n_0 \tau}$$

($1/a n_0$ is the effective life time for electrons in the conduction band). The two differential equations above give

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -\frac{n^2}{n_0 \tau}$$

which has the solutions

$$n = \frac{\tau n_0}{t + t_0}; \qquad \nu = \frac{1}{a(t + t_0)}$$

where t_0 is an integration constant equal to τ for saturation excitation, i.e. all traps filled at $t = 0$.

The luminescence intensity $I = a(n + \nu)\nu$ decays according to the simple law

$$I = \frac{\text{const.}}{(t + t_0)^2}$$

The equilibrium conditions are not necessarily valid throughout the decay, but are applicable after about 10^{-5} sec of decay.

This law is valid for the solution assuming equilibrium even if a distribution of trap depths is present. When the shallow traps reach equilibrium with deeper traps the system behaves as if the mean life time is single valued and equal to that of the deeper traps.

Thus the decay tends towards a final form, $I \propto t^{-2}$, according to the particular phosphor and excitation mechanism involved. This result is not in agreement with experiment. Often and at elevated temperatures we observe for ZnS(Cu) phosphors which give a linear $\log I - \log t$ plot with a slope greater than two. This constitutes one argument against the bimolecular formulation. However, this can always be attributed to simplified assumptions introduced into the calculations.

Adirowitch's theory. Adirowitch has considered the case for traps with a single mean life time τ, but where the capture cross-sections of empty centres and traps are not the same ($a_c \neq a_t$).

A rigorous solution is no longer possible, but Adirowitch has given an approximate solution for equilibrium conditions. He shows that a graph of $\log I$ as a function of $\log (t + t_0)$ has an inflexion and that there is an extensive range over which I follows a Becquerel type of relation:

$$I = \frac{\text{const.}}{(t + t_0)^p}$$

The table below gives various values of the index p for different values of the ratio $\gamma = \dfrac{a_t}{a_c}$

TABLE VI.3

γ	$\tfrac{1}{3}$	$\tfrac{1}{2}$	1	2	3	5	10	50	100	500
p	2·5	2·3	2	1·75	1·63	1·47	1·34	1·01	0·97	0·8

This type of formula is often a very good description of the decay of a number of phosphors over a considerable range. However, several objections have been made to Adirowitch's theory, among them being the following:

(i) The values of γ are often unacceptable, e.g. Coustal found $p = 0.43$ for a zinc sulphide phosphor at liquid air temperature which necessitates a γ value greater than 1,000.

(ii) In the case of a phosphor containing well-separated groups of traps the Becquerel formula is no longer suitable and a 'kink' is observed in the $\log I$ vs. $\log t$ curve (see Fig. VI.3).

Differential equations similar to those given above but rather more complex have been considered, for example, by Schön, by Broser and Broser-Warminsky and by Urbach, which include in the bi-molecular kinetics

(i) the distribution of trap life times,

(ii) non-radiation recom-binations,

(iii) positive hole migration in the valence band, their capture by activa-tor centres and the transfer processes which result.
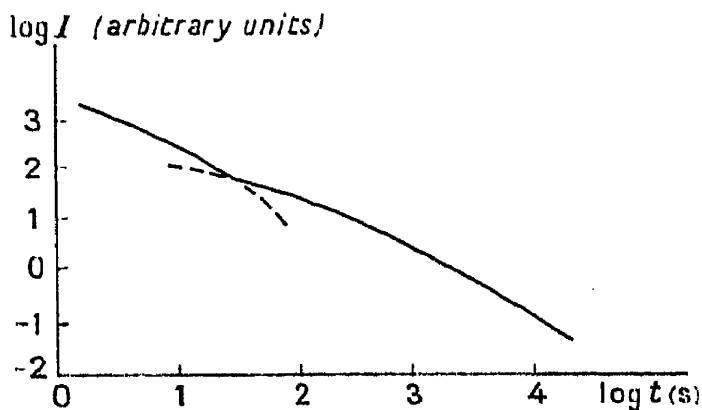

Fig. VI.3 *Decay of a wurtzite type ZnS(Cu) phosphor obtained by A. Guntz*

In conclusion, it is clear that the interpretation of phosphorescence decay is so complex that the decay cannot be used to infer the specific mechanism or processes involved. The early workers thought that it was sufficient to distinguish between equations of the type

$$\frac{dn}{n} = -\alpha\, dt$$

leading to a simple exponential decay, and

$$\frac{dn}{n} = -\alpha n\, dt$$

leading to a power law decay $I \propto t^{-2}$. However, each individual result can (by suitable assumptions about distributions and filling of traps) be interpreted in terms of a mono- or bi-molecular mechanism.

For instance, the Becquerel type of formula (as above) can be given a 'monomolecular' interpretation if we assume† a distribution of trap life times of the form

$$n_{0\tau} \propto \frac{1}{\tau^p}\, e^{-t_0/\tau}$$

In a specific case we obtain for $p = 2$ a hyperbolic decay which corresponds to that for a bimolecular mechanism with a single trap depth (we shall use this result later).

However, in spite of these remarks, other experimental data do

† For a discussion of phosphorescence mechanisms see 'Questions actuelles en luminescence cristalline', *Revue d'Optique*, Paris (1956), pp. 39–48.

give indications of the particular kinetics of phosphorescence. Thus in the case of ZnS(Cu) phosphors:

(1) No disagreement has been found between the trap distributions obtained from decay curves at different fixed temperatures by assumption of monomolecular kinetics and the trap distributions indicated more directly by thermoluminescence curves.

(2) Although electrons are raised into conduction levels by excitation (as shown by the occurrence of marked photoconduction closely related to the luminescence) during phosphorescence these electrons have energies only of the order of kT (polarons). Now it is usually assumed that the fraction of conduction electrons captured by crystal defects is much greater when the electrons are slow (see Fig. VI.4). Thus in an imperfect crystal, such as ZnS(Cu), we may assume that the 'floor' of the conduction band has irregularities, each of these being due to a defect. Shockley has shown that we can consider the energetic position of the bottom of the conduction band to provide an effective potential in which the electron is 'immersed'.

Energetic electron

Slow electron $E \simeq kT$

E

Fig. VI.4 *Electron potential in the conduction band. E is the kinetic energy of the electron*

The fast electrons will be unaffected by the irregularities, but slow electrons will be stopped. So we see that in phosphorescence the conduction electron displacements are very small but can become large if

(i) the crystal is reasonably perfect,

(ii) a strong accelerating electric field is present,

(iii) the electron energies are much greater than kT, i.e. for excitation, optical stimulation, or for electroluminescence.

(3) Electron retrapping has been found to be small during normal phosphorescence decay (not more than 10 per cent of the escaping electrons being retrapped), but it is much more marked for optical stimulation (more than 50 per cent for deep traps and almost 100 per cent for shallow traps). These figures are only the orders of magnitude for the effects in ZnS(Cu) and are valid at long decay times, i.e. when most of the traps are empty. The retrapping effect is much less marked when most of the traps are occupied. In addition, it has been found that the better the crystalline state of the phosphor the greater are the retrapping effects.

(4) The traps responsible for long-period phosphorescence in ZnS(Cu) phosphors occur when the 'green' centres due to copper impurity are introduced and the simplest assumption is that traps and centres are closely related, both being due to the introduction of copper. We are thus led to conclude that monomolecular kinetics will apply (i.e. traps localized around emission centres and excited electrons showing very small displacements). All this assumes excitation of electrons directly from centres which is true for ZnS(Cu) phosphors excited by 3,650 Å radiation. The electron excited from the centre falls into a neighbouring trap and similarly returns from that trap to the same centre to give emission. This allows the approximation to a monomolecular mechanism.

However, if excitation takes place in the fundamental absorption band of the crystal lattice, conditions are no longer the same. If the resulting electron and positive hole migrate independently of one another they will fill a trap and empty an emission centre respectively, the two not being in general near to each other. In this case the phosphorescence will be more characteristic of a bimolecular mechanism. This is the case for zinc sulphide excited by radiation of wavelengths less than 3,350 Å, or in the case of cadmium sulphide less than 5,100 Å. As a result we can arrange the following table:

TABLE VI.4

Dependence of recombination kinetics for electrons and empty centres in a photoconducting phosphor on experimental conditions

Nature of process		Electron displacement	Recombination kinetics
Electrons freed from traps by thermal activation: traps close to centres	Long-period phosphorescence and thermoluminescence	Small $< 10^{-6}$ cm	Approximately monomolecular
Electrons freed from traps or centres by optical activation	Stimulation: excitation of luminescence	Larger	Complex: monomolecular with perturbations
Excitation in fundamental lattice absorption band Electrons freed from traps not near to centres	Short-lived decay	Larger	Complex: bimolecular with perturbations
Nearly perfect crystals Electrons accelerated by electric field	Electroluminescence injection emission	Very large $> 10^{-5}$ cm	Approximately bimolecular

3. Investigations of trap distributions by analysis of experimental decay curves $I(t)$

The analysis is usually made by use of the formula

$$I(t) = \int_0^\infty \frac{n_{0\tau}}{\tau} e^{-t/\tau} \, d\tau$$

which for the monomolecular mechanism relates the distribution of traps filled by excitation $n_{0\tau}(\tau)$ to the phosphorescence intensity $I(t)$.

As in the table above, we assume the monomolecular mechanisms to be valid for the long-period phosphorescence, which appears to be so for ZnS(Cu) phosphors. To be more exact, we assume a perturbation of a bimolecular kind which explains the photoconduction characteristics but which is too small to affect the luminescence. We look briefly at the end of this chapter at what happens if the mechanism is not mono-molecular to a good approximation.

In experiment $I(t)$ is measured over a reasonably long time so that the particular traps involved are nearly all emptied. This type of experiment has been carried out systematically for ZnS(Cu) phosphors by J. Saddy. $I(t)$ at ordinary temperatures must be measured over the time interval from a fraction of a second up to about three hours. If, for instance, only the first half-hour of decay is measured, the results are of little significance in obtaining the trap distribution. During these times the phosphorescence intensity falls considerably. Use of the naked eye with a visual photometer is possible because of the large sensitivity range of the eye. If a photomultiplier is used the sensitivity range of the apparatus has to be changed often.

As another possibility one can use the method of Lenard and Kuppenheim and obtain the *light sum* remaining after time t:

$$S(t) = \int_0^\infty I(t) \, dt = \int_0^\infty n_{0\tau} e^{-t/\tau} \, d\tau$$

a method particularly appropriate to CaS(Bi) phosphors which contain traps with mean life times greater than a month. In these cases the filling of traps corresponds to a 'light sum' stored in the phosphor, but this is released so slowly that the observed phosphorescence represents only a small fraction of it. A sudden warming will free electrons from all traps and give rise to thermoluminescence. A photovoltaic cell placed in front of the phosphor will indicate by a meter deflection of an electrometer an electric charge proportional to the light sum released by warming.

After one or other of these experiments has been carried out the determination of the trap depths is made in three stages:

(a) An analysis of the distribution $n_{0\tau}(\tau)$ of mean life times of the trapped electrons.

(b) A transformation of this distribution $n_{0\tau}(\tau)$ to give the trap depth distribution $n_{0E}(E)$.

(c) Interpretation of the results.

(a) To obtain from $I(t)$ or $S(t)$ the quantity $n_{0\tau}(\tau)$ requires the inversion of a Laplace transformation. This becomes interesting when we try to find a form for $n_{0\tau}(\tau)$ which gives a decay law for which we have an analytical form. There do not seem to be machines for inversion of the Laplace transformation such as exist for inversion of the Fourier transformation (harmonic analysers). In practice, we are reduced to using the method of calculation previously employed by Lenard and Kuppenheimer.

In order to get some idea of the problem, consider $S(t)$. We replace the integral, using an approximation, by a sum of exponential terms

$$S(t) = \Sigma\, n_{0\tau}(\tau)\, e^{-t/\tau}\, \Delta\tau$$

In other words, we break down the experimental decay curve into a series of exponential terms. We shall not describe the process of resolution into these terms, a current practice in nuclear physics,† but simply make the following observation:

The exponential terms for radioactive decay have a real significance; their exponents τ are the mean life times of the constituents. Different workers will obtain the same τ values which are not usually very numerous.

In the present case the exponential terms are only a convenience in calculation; the resultant trap distribution, which for sulphides is continuous, has only one meaning. The number of exponential terms and the values of τ depend on the precision involved in the resolution. It is wrong to consider the values as the life times of the trapped electrons. They simply provide points through which a graph of $n_{0\tau}(\tau)$ may be drawn.

The investigation of the convergence of the calculated distributions as the number of component terms becomes larger and larger gives the proper assurance of the validity of the deduced distribution.

(b) The trap depth E and not the mean life time τ is a better

† Joliot-Curie, I. (1946) *Les Radio-Éléments naturels*, p. 15. Hermann, Paris.

characteristic to define a trap since the mean life time depends on the temperature at which decay takes place:

$$\frac{1}{\tau} = s\, e^{-E/kT}$$

the change from $n_{0\tau}(\tau)$ to $n_{0E}(E)$ is made by putting $n_{0E}\, dE = n_{0\tau}\, d\tau$

$$E = kT \log (s\tau) \quad \text{and} \quad dE = kT\frac{d\tau}{\tau}$$

and so

$$n_{0E} = n_{0\tau}\frac{\tau}{kT}$$

To obtain the form of the trap distribution it is sufficient to plot the product $n_{0\tau}(\tau).\tau$ as a function of $\log \tau$. In order to obtain the trap depths it is necessary to obtain s. The most accurate way to do this is to follow the behaviour of each group of traps by measuring the decay at different temperatures (cf. Fig. VI.1). s may also be obtained from thermoluminescence experiments.

(c) *Results.* The trap distribution usually occurs as a collection of approximately 'Gaussian' groups (see Fig. VI.5). Each of these groups can be assigned a value of E corresponding to that of its maximum.
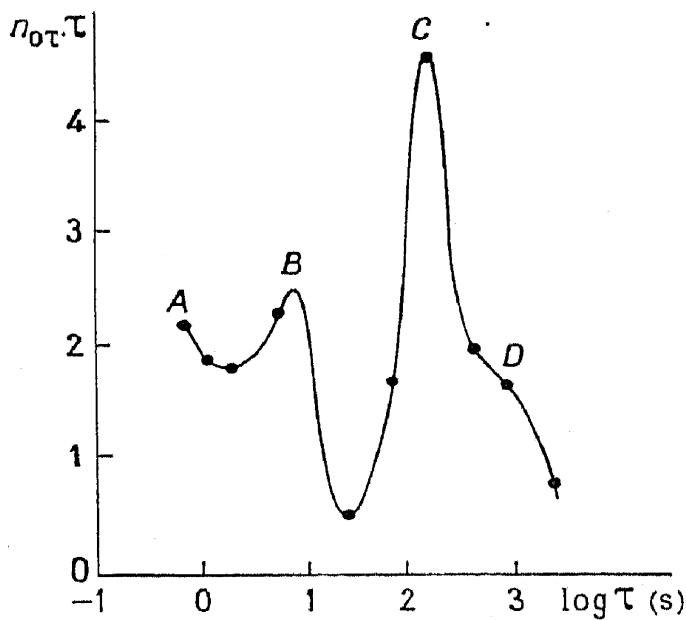
Fig. VI.5 *Trap distribution in a ZnS(Cu) phosphor with the decay curve of Fig. VI.3*

Mean life times and trap depths in ZnS(Cu) (wurtzite). If we denote the various maxima of the groups of traps in Fig. VI.5 by A, B, C and D respectively, then at room temperature we have

$$\log \tau(s) = 0.5 \text{ (for A), } 0.9 \text{ (for B), } 2.2 \text{ (for C), and } 3 \text{ (for D)}$$

and if $s \approx 10^9$ sec^{-1} the corresponding trap depths are

$$0.5,\ 0.57,\ 0.65 \text{ and } 0.7 \text{ eV respectively.}$$

In this specific case the gap between groups B and C is particularly marked, whence the 'kink' in the curve of Fig. VI.3, but the

same groups A, B, C and D are found for all long afterglow zinc sulphide phosphors. There are other groups, but they are so deep that they contribute little to the decay at room temperature. They can be found by means of thermoluminescence curve experiments, but they would have been noticed if the decay had been measured at other temperatures.

N.B. The above method of finding trap distributions assumes that the decay is monomolecular to a first approximation. If the decay is bimolecular then there are no satisfactory formulae available. However, even in this case we can, apparently, go on using the monomolecular formulae (1 above) without introducing serious errors.

Consider the case where a bimolecular treatment is needed and for a single trap depth. The actual trap distribution corresponds to a single mean life time t_0 with a corresponding trap depth E given by

$$\frac{1}{t_0} = s\, e^{-E/kT}$$

If, as seen previously, we assume the same capture cross-sections for centres and traps and neglect non-radiative transitions and positive hole migration, then decay of phosphorescence follows a simple bimolecular law

$$I = \frac{\text{const.}}{(t+t_0)^2}$$

and if excitation produces saturation, then t_0 is the mean life time of the trapped electrons. Ignoring the actual luminescence mechanism in such a phosphor, the experimenter interprets the decay in terms of a monomolecular mechanism and obtains an apparent life time distribution for the trapped electrons:

$$n_{0\tau}(\tau) = \frac{1}{\tau_0}\, e^{-t_0/\tau}$$

and deduces the trap depth distribution:

$$n_{0E} \propto n_{0\tau}(\tau)\,.\,\tau = \frac{1}{\tau}\, e^{-t_0/\tau}$$

The maximum of this apparent distribution occurs at $\tau = t_0$, i.e. at the position corresponding to the actual trap depth E. Thus the apparent distribution obtained differs from the real distribution, but the maxima for each coincide. This conclusion is only valid if the initial excitation saturates the trapping states.

III. THE METHOD OF THERMOLUMINESCENCE CURVES (OR GLOW CURVES)

1. Description of the method

This method, less precise than that of analysis of decay curves, is more convenient and more rapid. It was first proposed by F. Urbach and then by Katz and Solomoniouk, but its use is now extensive due to the researches of Randall and Wilkins.

The method is as follows:

(1) The phosphorescent solid is first excited at a low initial temperature T_i, low enough for the traps to be investigated, not to lose their electrons.

(2) The solid is warmed at a rate β which is made as uniform as possible.

The traps empty as the temperature rises, the 'shallow' ones first,
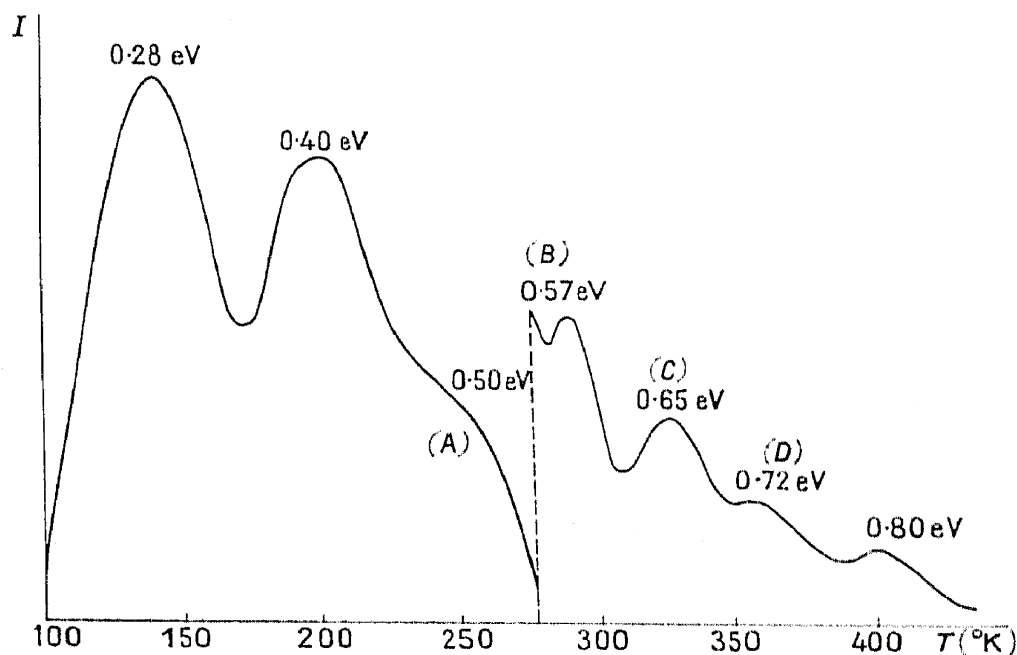
Fig. VI.6 *Thermoluminescence curve of a long afterglow ZnS(Cu) phosphor. The trap depths involved are indicated at each maximum. The letters* A, B, C, D *denote the groups of traps similarly indicated in Fig. VI.5 obtained from decay curves*

At 0°C the sensitivity of the apparatus was increased sevenfold

The groups A, B *and* C *are complex and sometimes can be resolved into subgroups (see Fig. VI.7)*

and at each temperature T those with life times of a fraction of a second or so are principally responsible for the observed thermo-

luminescence. If there is only one trap depth, then the thermoluminescence is very weak at $T = T_i$; but then increases with T, reaches a maximum for the *temperature of thermoluminescence, T^**, and then decreases to zero as the traps are all emptied. If the trap distribution consists of separate groups of trap depths, then these groups are observed as thermoluminescence maxima. The problem is: Knowing the temperature T^* of maximum thermoluminescence, what is the trap depth E involved.

Urbach gave the approximate numerical relation

$$E \, (\text{eV}) = \frac{T^*(°\text{K})}{500}$$

deduced from experiments on KCl(Tl): this formula gives the right order of magnitude of E for a number of phosphors.

2. Simple theory of the thermoluminescence curve due to Randall and Wilkins

This theory assumes a monomolecular mechanism as used above for phosphorescence, i.e. it stems from the equation:

$$\frac{dn}{dt} = -\frac{n}{\tau}, \qquad I = \left| \frac{dn}{dt} \right|$$

where n is the number of traps filled at time t and τ is the mean life time of the trapped electrons, I being the thermoluminescence intensity.

Previously τ was a constant, the temperature being fixed, but now T increases with the time t according to the relation

$$dT = \beta \, dt$$

and so τ also varies:

$$\frac{1}{\tau} = s \, e^{-E/kT}$$

and n is given by the integration

$$n = n_0 \exp\left[-\int_0^t \frac{1}{\tau(t)} \, dt \right] = n_0 \exp\left[-\int_{T_i}^{T} s \, e^{-E/kT} \frac{dT}{\beta} \right]$$

n_0 being the number of filled traps at time $t = 0$ (at beginning of heating).

The thermoluminescence intensity $I(T)$ at the temperature T is given by

$$I(T) = n_0 s \exp\left(-E/kT \right) \exp\left[-\int_{T_i}^{T} s \exp\left(-E/kT \right) \frac{dT}{\beta} \right]$$

A constant warming rate need not be used† and the work of T. Louchtchik shows the interest in a different heating regime (heating in 'bursts'). However, T^* for maximum emission depends on the rate of heating and we shall here assume β to be constant.

The above formula gives by numerical integration the complete form of the thermoluminescence curve, but the calculations are laborious and often an attempt is made to deduce the depth E from T^*. T^* is found by setting $dI/dT = 0$ and this gives

$$\beta \frac{E}{kT^{*2}} = s\, e^{-E/kT^*} \tag{2}$$

E is thus an implicit function of T^*, the relation between them being defined by the parameter $\theta = \beta/s$. From numerical calculations this relation can be obtained with sufficient accuracy (better than 1 per cent) and we can write

$$E\,(\text{eV}) = \frac{T^*(^\circ K) - T_0(\beta/s)}{K(\beta/s)} \tag{3}$$

the values of T_0 and K being obtained graphically and given in the following table:

TABLE VI.5

$\theta = \beta/s\ (^\circ K)$	$K\ (^\circ K/eV)$	$T_0\ (^\circ K)$
10^{-4}	833	35
10^{-5}	725	28
10^{-6}	642	22
10^{-7}	577	17
10^{-8}	524	13
10^{-9}	480	10
10^{-10}	441	7
10^{-11}	408	6
10^{-12}	379	6
10^{-13}	353	5
10^{-14}	331	5
10^{-15}	312	4

For ZnS(Cu) phosphors, where s is about 10^9 sec^{-1}, the Urbach formula $E \approx T^*/500$ gives the right order of values for relatively

† More recently (1958), M. Schön has shown that the use of a heating rate such that $1/T$ is a linear function of the time t, i.e.

$$d(1/T) = -\beta\, dt$$

leads to integrations that may be easily carried out in terms of simple exponential functions.

high warming rates of about 1°K/sec.† However, slower warming is often used to get a better separation of the different groups of traps and to be less affected by thermal capacity effects. For $\beta \approx 0.01°$K/sec, $E \approx T^*/400$. The formula (3) is precise, but the major problem lies in the determination of s.

3. Thermoluminescence curve measurements using two different warming rates

Booth, Bohun and also Parfianovitch have shown independently that the need to know s can be avoided if one uses two different warming rates, β_1 and β_2, to obtain E. The same trap depth then results in two different values of T^*, i.e. T_1^* and T_2^*. If $\beta_1 > \beta_2$, then $T_1^* > T_2^*$.

By using the equation (2) above the elimination of s gives

$$\frac{E}{k}\left(\frac{1}{T_2^*}-\frac{1}{T_1^*}\right) = \log\left(\frac{\beta_1}{\beta_2}\cdot\frac{T_2^{*2}}{T_1^{*2}}\right)$$

from which E can be obtained. If we now want to know s we can write (A. Wrzesinska)

$$\log\frac{sk}{E} = \frac{T_2^* \log\dfrac{T_2^{*2}}{\beta_2}-T_1^* \log\dfrac{T_1^{*2}}{\beta_1}}{T_1^*-T_2^*}$$

Unfortunately the above method, which is most convenient, is not very precise, since T^* varies so little with warming rate: E can only be estimated with a 20 or 30 per cent accuracy.

4. Observations on thermoluminescence equations

As in section II, for the decay we can obtain the thermoluminescence equations based on a bimolecular mechanism and then show that the assumption of monomolecular basis as in the Randall–Wilkins theory does not lead to any serious errors in determining the trap distribution.

We assume a single trap depth and equal capture cross-sections for centres and traps. We use the differential equation as for decay (see

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† Randall and Wilkins have shown that the mean life T is little different from 1 sec at the glow temperature T^*:

$$E = kT^* \log_e s[1+f(s, \beta)]$$

This is a coincidence, valid in ZnS for high values of the heating rate, but it is not generally valid. The formula

$$E = kT \log_e (s)$$

(obtained by putting $f(s, \beta) = 0$) is a poor approximation. Urbach's simple formula is better.

page 151 above). However rapid the warming rate, the phosphor temperature will be sensibly constant for the time ($\approx 10^{-5}$ sec) taken to establish equilibrium between the trapped electrons and those in the conduction band. We thus use the equation

$$\frac{dn}{dt} = \frac{-n^2}{n_0\tau}$$

Since we now have T, and also as a result τ, varying with time, the integral of the equation must be written

$$n = \frac{n_0}{1+\int_0^t \frac{dt}{\tau}} = \frac{n_0}{1+\int_{T_i}^T s \exp\left(-E/kT\right) dT/\beta}$$

Assuming excitation saturates the traps initially, the thermoluminescence intensity $I = |\, dn/dt\,|$ and at time t or temperature T:

$$I(T) = n_0 s\, e^{-E/kT} \Big/ \left[1+\int_{T_i}^T s \exp\left(-E/kT\right) dT/\beta\right]^2$$

The temperature for the emission maximum is given by $dI/dT = 0$, and so

$$\beta\frac{E}{kT^{*2}}\cdot\frac{1}{2}\left[1+\int_{T_i}^T s \exp\left(-E/kT\right) dT/\beta\right] = s \exp\left(-E/kT^*\right) \quad (2a)$$

This relation differs from that of (2) by the factor

$$\frac{1}{2}\left[1+\int_{T_i}^T s \exp\left(-E/kT\right) dT/\beta\right] = \frac{n_0}{2n^*}$$

where n^* is the number of electrons left in traps at T^*. The thermoluminescence curve is not quite symmetrical and the change from T to T^* does not correspond exactly to the relation $n^* = n_0/2$. However, the difference is not large and T^* is only changed by a per cent or so by the above factor (A. Wrzesinska).

So we see that the application of monomolecular formulae (3) to T^* gives an approximately correct value for the maximum of the trap distribution, but if the whole curve is plotted, then the bimolecular formula gives a wider apparent distribution than really exists.

T. Louchtchik in his book *Crystal Phosphors* has given many numerically obtained thermoluminescence curves for mono- and bimolecular theory and for various values of E, S and β. He has also investigated the variation of radiative emission probability with temperature

$$\eta(T) = \frac{\eta_0}{1+C \exp\left(-W/kT\right)}$$

in relation to its effect on thermoluminescence curves. In the region where thermal quenching is large the temperatures T^* of maximum thermoluminescence emission have lower values than where thermal quenching is absent. The shift can reach as much as $10°$, which is greater than the error in measuring T^*. For monomolecular processes we can make the simple correction for thermal quenching:

$$I(T)_{observed} = I(t)_{real} . \eta(T)$$

but the correction becomes complex in the bimolecular case. If thermal quenching is marked ($T^* > 200$ or $300°C$ for ZnS), the traps involved do not show up in the thermoluminescence curve.

By use of the same kind of mathematical approximations as those in Adirowitch's theory for decay (i.e. the 'quasi-stationary' approximation), Louchtchik and co-workers have extended their calculations to the bimolecular mechanism when the ratio $\gamma = a_t/a_c$ of the electron cross-sections for traps and centres is not unity. When the retrapping probability is much larger than the recombination probability ($\gamma \gg 1$), a quasi-monomolecular approximation is obtained. Thus in the region for $\gamma > 1$, the Randall–Wilkins formula gives rather good results, as a general rule, for the case of saturation excitation. But if γ is appreciably smaller than unity, the peak glow temperatures calculated by Louchtchik are somewhat higher.

IV. DATA ON ELECTRON TRAPS IN VARIOUS PHOSPHORS

1. ZnS(Cu) phosphors

The mean values of E for different groups of traps as formed by various workers indicate a close correlation between thermoluminescence curves and phosphorescence decay curves. Similar trap depths are apparently found in spite of the particular method of preparation of the sulphides. Thus Joukova has found that the use of fluxes such as LiCl, NaCl or KCl modifies the relative importance of the different groups of traps but not their mean depths.

We give here some results of this.

(a) A group of traps with E about 0.28 eV occurs which is independent of the activator centre: this can be explained in terms of a hydrogenlike model of localized states (Bethe model). According to this model the electron moves in a field due to a substitutional charge $+e$ in the lattice (possibly a sulphur vacancy). In the ground state it

will move in a Bohr orbit of radius $a = Ka_0$ ($a_0 = 0.53$ Å) and its energy is $-R/K^2$ ($R = 13.5$ eV), a value which gives the trap depth below the conduction band.

In a covalent crystal K is the dielectric constant of the medium. In an ionic crystal the static (K) and optical (K_0) dielectric constants are different and the ionic polarization must be considered. Thus *an effective dielectric constant K_e is introduced* given by

$$\frac{1}{K_e} = \frac{1}{K} + \frac{5}{16}\left(\frac{1}{K_0} - \frac{1}{K}\right)$$

The orbital radius is $a = K_e a_0$ and the thermal activation energy is

$$E = \frac{R}{K_e^2}$$

The optical activation energy is (see Chapter VII)

$$hv = \frac{R}{K_e}\left(\frac{15}{16}\frac{1}{K_0} + \frac{1}{16}\frac{1}{K}\right)$$

or approximately

$$hv \approx \frac{R}{K_e K_0}$$

TABLE VI.6

Numerical values for various ionic crystals

	K	$K_0 = n^2$	K_e	E (eV)	hv (eV)
ZnS	8·3	5·07	6·93	0·28	0·38
CdS	11·6(?)	5·85	8·88	0·17	0·26
ZnO	12 (?)	3·88	7·25	0·26	0·47
Cu$_2$O	9	4·0	6·48	0·32	0·50

In ZnS, CdS and ZnO thermoluminescence gives peaks corresponding to 0·28, 0·17 and 0·26 eV. In Cu$_2$O the activation energy for semiconduction indicates a level with $E = 0.32$ eV (acceptor level). Thus the agreement with experiment is very good, in fact so good that it must be fortuitous.

The above values were found by R. Freymann and his collaborators for the activation energies involved in Debye-type dipolar absorption.

(b) A group of traps with $E \approx 0.4$ eV found by Garlick and also by Wallick to be pronounced in fine grain size sulphides and attributed to surface traps.

(c) An assembly of trap groups associated with introduction of copper.

The model which is described below leads to the following trap depths :†

TABLE VI.7

Trap depths E and the corresponding mean life times τ at room temperature (18°C), computed for s = 10⁹ sec⁻¹

	E (eV)	τ(s)
(A)	0·48	0·2
	0·50	0·45
	0·53	1·5
(B)	0·565	6·0
(C)	0·61	38
	0·63	81
	0·68	600
(D)	0·715	2,500
	0·815	120,000

The groups (A), (B) and (C) are generally not resolved into the subgroups predicted by the model (see Figs. VI.5 and VI.6). Such a
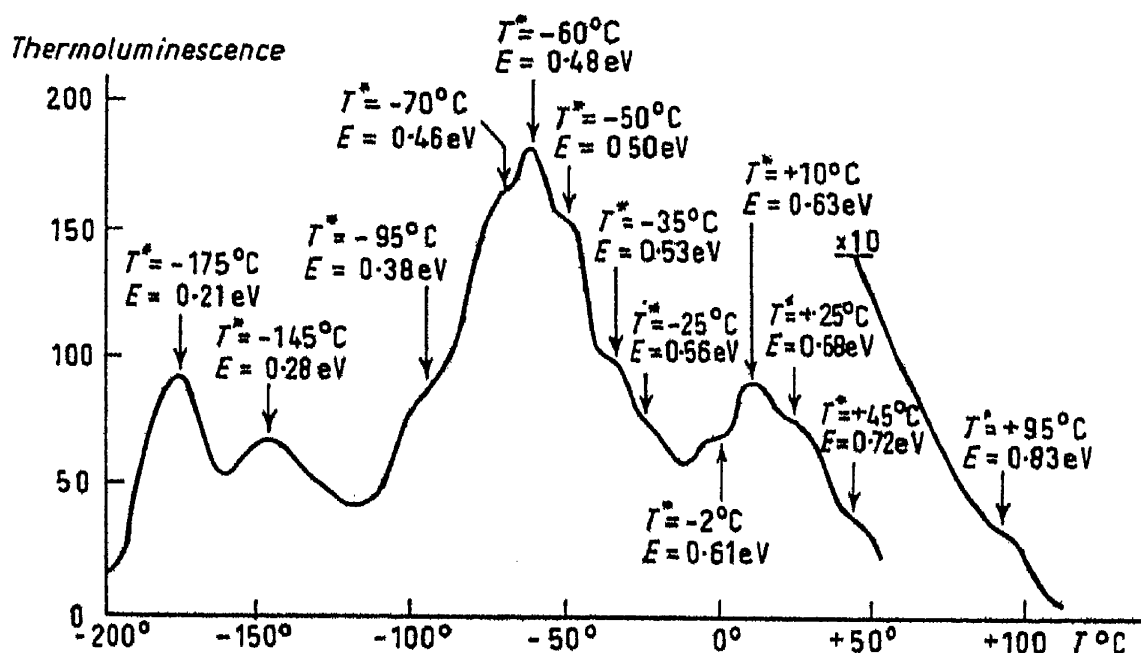
Fig. VI.7 *Glow curve of a ZnS(Cu) phosphor fired at 1,150°C. Heating rate β = 0·06°/s. The trap depths are computed by the formula (see page 162)*

$$E\,(eV) = \frac{T^*(°K)-7}{433}$$

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† At present the traps which have been found from the thermoluminescence curve are

(a) the traps corresponding to the six nearest neighbours;

(b) for larger distances the most important groups, i.e. those common to blende- and wurtzite-type phosphors.

resolution of the glow peaks needs a convenient choice of the rate of heating β; in addition, this rate must be maintained at a constant value during the glow experiment with a degree of accuracy.

The traps with $E \approx 0.8$ eV lose their electrons very slowly at room temperature and give rise to no appreciable phosphorescence. However, the groups with $E = 0.57$ and 0.61 to 0.68 eV (which occur in both cubic and hexagonal ZnS) and with $E = 0.72$ eV (in hexagonal ZnS) give the long duration phosphorescence of ZnS at ordinary temperatures.

These traps can be associated with the charge $+$e of the level of (*a*) above perturbed by the nearness of the copper centre which functions as a second substitutional charge $+$e when it is ionized (i.e. after excitation). Using the hydrogenlike model, this trap model describes the trapped electron as captured in the field of two positive charges ($+$e) A and B, one being a sulphur vacancy (A) and the other (B) being the singly ionized luminescence centre at a zinc site. The depth of such a trap is given approximately by

$$hv \approx \frac{R}{K_e{}^2} + \frac{e^2}{K r_{AB}}$$

where K_e is the effective dielectric constant as defined previously in (*a*) above and K is the static dielectric constant. The term $e^2/K r_{AB}$ gives the perturbation of the simple trap depth $E = R/K^2$ when there is a second charge $+$e at a distance r_{AB} from the first.

The same perturbation is effective in the expression for the optical activation energy, which is thus the same degree of approximation:

$$hv \approx \frac{R}{K_e K_0} + \frac{e^2}{K r_{AB}}$$

The above formulae are not accurate. A more rigorous treatment has been given (D. Curie, 1957), using the LCAO method for describing the trapped electron.

Knowing the coordinates of the zinc and sulphur atoms in the cube (blende) or hexagonal (wurtzite) lattices, it is simple to obtain r_{AB} as shown in the table.

We notice the agreement between the calculated and observed values for the thermal activation energy E. In particular we find also that the same distance r_{AB} applies to the two different crystalline forms and the same trap depths. In addition, for wurtzite the distance $r_{AB} = 5r_0/3$ gives the corresponding trap depth of 0.72 eV, giving the

TABLE VI.8

Trap depths according to the hydrogen molecular-ion model

Blende		Wurtzite		ZnS		CdS	
Number of sites	r_{AB}	Number of sites	r_{AB}	E (eV)	$h\nu$ (eV)	E (eV)	$h\nu$ (eV)
4	1	4	1	0·815	0·96	0·475	0·60
		1	5/3	0·715	0·84	0·425	0·53
12	$\sqrt{11/3}$	9	$\sqrt{11/3}$	0·68	0·80	0·41	0·51
		6	7/3	0·63	0·75	0·39	0·48
12	$\sqrt{19/3}$	9	$\sqrt{19/3}$	0·61	0·72	0·38	0·46
16	3	9	3	0·565	0·67	0·36	0·45
		3	$\sqrt{89/3}$	0·55	0·65	0·355	0·445
		6	$\sqrt{97/3}$	0·54	0·63	0·35	0·44
24	$\sqrt{35/3}$	18	$\sqrt{35/3}$	0·53	0·62	0·34	0·43
		3	$\sqrt{113/3}$	0·52	0·605	0·34	0·425
		7	11/3	0·51	0·595	0·335	0·42
12	$\sqrt{43/3}$	3	$\sqrt{43/3}$	0·50	0·585	0·33	0·41
		6	$\sqrt{137/3}$	0·49	0·575	0·32	0·40
24	$\sqrt{17}$	12	$\sqrt{17}$	0·48	0·56	0·315	0·395

The distances r_{AB} are given in units of $r_0 = 2·35$ Å for ZnS and $n_0 = 2·52$ Å for CdS; r_0 is the distance between nearest neighbours.
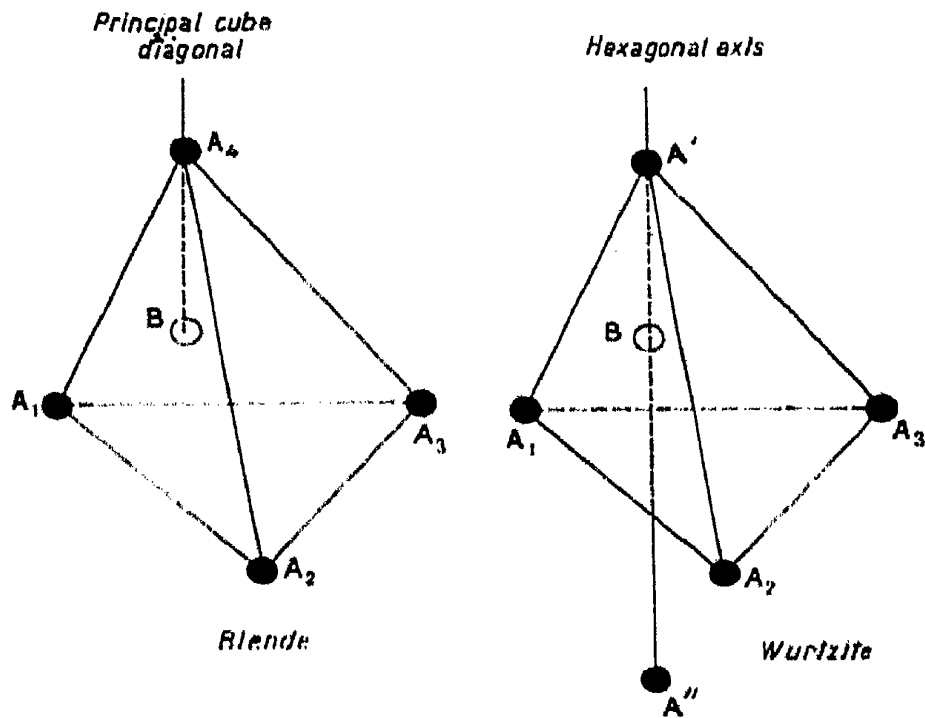
Fig. VI.8 *Position of nearest neighbour sulphur atoms relative to zinc atoms in the blende and wurtzite lattices of ZnS*

A *sulphur*   B *zinc*

longer phosphorescence for the wurtzite lattice phosphor than for the blende lattice specimens.

In the blende crystals the zinc and sulphur atoms are arranged in a face-centred cubic lattice, while in wurtzite they occur on a compact hexagonal lattice. In blende, as in wurtzite, a zinc atom B (see Fig. VI.8) is surrounded by four sulphur atoms at a distance r_0, forming a tetrahedron with zinc at the centre. In wurtzite, however, the four sulphur atoms are not equivalent. If the hexagonal axis is vertical, then three of the atoms A, A_2 and A_3, form an equilateral triangle in the horizontal plane while the fourth A' is directly above the zinc atom a distance r_0 away along the axis. If $b = 8r_0/3$, the spacing along the hexagonal axis, the sulphur atom A'' below b has a distance $r_{AB} = 5r_0/3$, and this gives the extra trap depth 0·72 eV.

(*d*) Finally, for ZnS a number of very shallow traps exist ($E = 0·1$ eV) which have very short life times for electrons except at very low temperatures (N. Riehl).

2. CdS phosphors

The traps in CdS are shallower than in ZnS and less well separated because of the higher value of K. It seems possible to resolve only the following groups:

$$E = 0·475 \text{ eV}, \quad E \approx 0·42 \text{ eV}, \quad E \approx 0·35\text{--}0·39 \text{ eV}, \quad E \approx 0·17 \text{ eV}$$

This seems to be in agreement with Bube's, with Broser-Warminsky and with Boer's experimental results. In order to obtain the best agreement between calculated and experimental values, one must accept a lower value of the parameter s in CdS than in ZnS:

$$s \approx 10^8 \text{ sec}^{-1} \text{ in CdS} \qquad s \approx 10^9 \text{ sec}^{-1} \text{ in ZnS}$$

The total number of deep traps ($\tau > 1$ minute) in zinc and cadmium sulphides seems to be of the order of 10^{15} per cm³ (H. Kallmann, Spruch and Sucov). The number of shallow traps is probably larger by one or two orders of magnitude. Some experiments give evidence for a considerable amount of retrapping in short-lived traps.

These figures may be compared with the number of luminescence centres. In a zinc sulphide phosphor activated with copper at the optimum concentration of $2 \cdot 10^{-4}$ g Cu/g ZnS, the number of centres is about $4 \cdot 10^{18}$ per cm³.

3. CaS(Bi) phosphors

Calcium sulphide is one of the oldest known phosphorescent materials having a fine violet luminescence and a very long afterglow (Balmain's paint). Its composition is not well defined and it usually contains some CaO, $CaCO_3$ and $CaSO_4$. Traps of many different depths are usually found for this phosphor. The principal groups deduced from phosphorescence light sums at room temperature (Lenard), have mean life times of 10^7, $10^{5.6}$ and $10^{3.3}$ sec corresponding to trap depths ($s \approx 10^{10}$/sec) of 1, 0·9 and 0·8 eV. These appear to be independent of activator centre concentration (Lenard and Kuppenheim). The thermoluminescence peaks at a temperature of about 400°K, but there are indications of a trap group with $T^* \approx 550°C$ giving $E \approx 1·2$ eV, the mean life times being of the order of *centuries* at room temperature. The latter group seems to be associated with the introduction of bismuth impurity (A. F. Wells).

4. KCl(Tl) phosphors

We have already given the energy-level scheme for the thallium ion (see Fig. II.3). While the states $^3P_1$ and $^1P_1$ give rise to the principal absorption and emission bands, the states $^3P_0$ and $^3P_2$ are metastable and form the trapping levels. Absorption at 2,500 Å raises the ion from the ground state $^1S_0$ to the excited state $^3P_1$, from whence the electron can fall back to the $^1S_0$ state with emission at 3,050 Å or be captured into the metastable state $^3P_0$ (or be transferred to the $^1P_1$ state).

A thermal or suitable optical activation can raise the Tl^+ ion from the trapping state $^3P_0$ to the state $^3P_1$ to give subsequent emission ($^3P_1-^1S_1$). Such a trap system will give an essentially monomolecular mechanism for phosphorescence which will follow an exponential law with a single life time τ. Bünger and Flechsig measured the light sum $S(t)$ and for certain crystals of KCl(Tl) (which they called 'good' crystals) found that

$$S(t) = S_0 e^{-t/\tau} + \text{const.}$$

the latter constant being due to the effect of deeper traps. The life time satisfies the usual relation

$$\frac{1}{\tau} = s e^{-E/kT}$$

with $E = 0·67$ eV and $s = 2·9 \times 10^9$ sec^{-1}. In the so-called 'good'

crystals (apart from the very shallow and very deep traps) a group with a life time very closely centred on a single value was found.

However, if this group is 'wide' due to different interactions of different Tl$^+$ ions with the crystal lattice, then the decay is no longer of simple exponential form. Bünger and Flechsig called crystals with such groups of traps 'bad' crystals.

Thermoluminescence curves provide more precise information. For low Tl$^+$ ion concentrations only two maxima appear (see Fig. VI.9), which are much larger than those of phosphorescent sulphides. The most important of these occurs at $T^* = 300°K$ $(\beta \approx 2\cdot5°/sec)$ and the formulae (3) of section III enable this to be identified with the trap
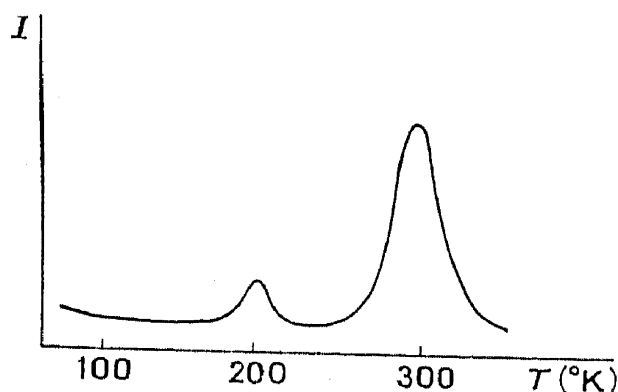
Fig. VI.9 *Thermoluminescence curve for KCl(Tl) (thallium concentration 0·05 per cent: $\beta = 0\cdot83°K/sec$) (After Johnson and Williams)*

investigated by Bünger and Flechsig and their value of s is confirmed. The second maximum at $T^* = 205°K$ gives $E \approx 0\cdot4$ eV.

Johnson and Williams have shown that these traps are due to the metastable states $^3P_0$ and $^3P_2$ of the thallium ion. They studied the variation of thermoluminescence intensity with thallium ion concentration, which varies in the same way as the luminescence, and on this they based their conclusions. When the concentration is high other thermoluminescence maxima occur, in particular a peak at $T^* = 250°K$ due to pairs of adjacent Tl$^+$ ions (F. Seitz).

Only specimens of KCl(Tl) prepared from the melt show such trap distributions having a restricted and well-defined number of groups. P. Pringsheim has prepared different specimens by precipitation from saturated aqueous solutions which show an excellent luminescence, but the thermoluminescence shows no pronounced maxima which indicates a wide distribution of trapping levels.

5. Thermoluminescence of alkali halides with colour centres

If the temperature is raised, colour centres of *F*, *M*, *R* types, &c. (vacancies with one or more charge carriers) lose their electrons and behave like electron traps. If the freed electrons reach luminescence centres, then a thermoluminescence peak results. The observed emission is usually in the ultra-violet or in the blue region of the spectrum and may be due to transitions in *V* centres or in impurity centre (see page 64). The thermoluminescence is accompanied by remarkable effects, but these are difficult to interpret:

(*A*) The thermal activation of a colour centre causes a bleaching of the corresponding absorption band at the same temperature as that for thermoluminescence (Pringsheim and Yuster, T. Louchtchik, &c.).

(*B*) The ultimate capture of the liberated electron by a vacancy gives rise to another absorption band (at the expense of the first).

(*C*) The capture of the electron in a *V* centre (positive ion vacancy containing a positive hole) causes a bleaching of *V* centre absorption simultaneously with the bleaching of the original colour centre band.

Similar effects have been observed in conventional phosphors such as ZnS and CdS (Halperin and Garlick), but the absorption bands due to traps in the sulphides are in the infra red between 1 and 3 μ rather than in the visible as for colour centres in alkali halides.

(*D*) As far as the emission spectra are concerned an electron coming from an *F* centre, for example, can recombine with different luminescence centres. Thus thermoluminescence emissions of different colours may arise from the thermal emptying of the same trap (Bonfiglioli, Brovetto and Cortese).

On the other hand, the emptying of different traps may be followed by the recombination of the conduction electrons and of holes in the same luminescence centre; and so we obtain different thermoluminescence peaks with the same emission spectra (Halperin, Kristianpoller *et al.*).

Here we give a typical example:

In KCl the *F*-band absorption is at 2·55 eV in the green-yellow region and so a KCl crystal with colour centres has a deep blue or rather *magenta* colour. Bose and Sharma bombarded KCl with cathode rays at liquid air temperature but not many *F* centres were produced, the crystals acquiring a rose tint due to unidentified colour

centres. By heating the crystals at a uniform rate a thermoluminescence curve was recorded (see Fig. VI.10) with two main peaks at $T^* = 205°K$ and $T^* = 620°K$.

When the first peak was passed through the rose coloration disappeared and at the same time the 'magenta' colour characteristic of recapture of electrons in vacancies to form F centres was observed. This coloration persisted up to 620°K, when the crystal bleached during the emission of the second glow peak.

If we take 620°K as the thermoluminescence temperature corresponding to the thermal activation of F-centre electrons, then use of
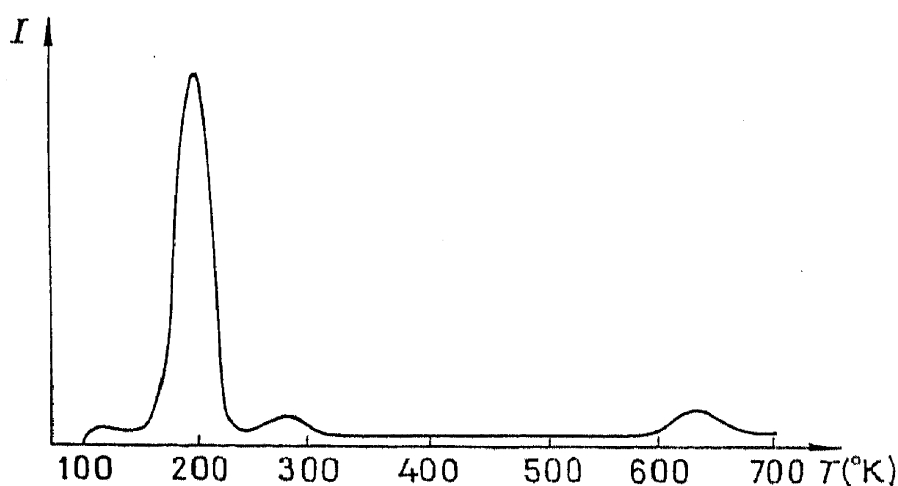
Fig. VI.10 *Thermo luminescence curve of KCl (no thallium) after cathode-ray excitation at 90°K ($\beta = 5°$—$6°$/sec)*
(After Bose and Sharma)

the relation $E = T^*/500$ gives $E \approx 1·2$ eV, assuming $s = 10^{10}$ sec^{-1}. Other workers (Parfianovitch) have suggested an s value of 10^{14} sec^{-1}, which gives $E \approx 1·8$ eV, and this is theoretically preferable.†
We thus have:

F-band absorption in KCl at 0·55 μ	$h\nu \approx 2·3$ eV
F-band emission in KCl at 1·00 μ	$h\nu = 1·4$ eV
Thermal activation energy	$E \approx 1·8$ eV

The thermal energy E is markedly less than the optical activation energy of 2·3 eV as predicted by Mott.

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† The configurational coordinate model (see Chapter VII) leads to the inequality

$$h\nu_{\text{emission}} < E_{\text{thermal}}$$

being obeyed for an E value of 1·8 eV rather than 1·2 eV.

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Thermal and Optical Activation of

Trapped Electrons: Quenching Effects

I. TRAPS, THERMAL ACTIVATION AND OPTICAL STIMULATION IN THE CONFIGURATIONAL COORDINATE MODEL

1. Description of the escape from traps

This type of model is particularly applicable when trapping processes are confined together with luminescence transitions within an atomic or ionic activator centre: the example of KCl(Tl) has already been quoted. The energy of the trapping state in interaction with the lattice is given by a configurational coordinate curve $\mathscr{U}^g(r)$ when the system is in the ground state and by $\mathscr{U}^e(r)$ when it is raised into the short-lined excited state from which a luminescence transition may take place.

We can also employ a configurational diagram when the electrons escaping from traps enter the conduction band. Certain difficulties met with in studying the capture cross-sections of traps suggest the assumption that capture and subsequent activation involve the transition through a very shallow level. In this case $\mathscr{U}^g(r)$ applies to the ground state and $\mathscr{U}^e(r)$ to the shallow excited level and there is no problem in applying the configurational coordinate model. If, on the other hand, the emptying of traps raises the electron directly into the conduction band, following R. Kubo we can use $\mathscr{U}^e(r)$ to denote the potential energy of the system 'trap+lattice' when the electron has just left the trap and is in the conduction band. The 'ionization continuum' is then given by all the energies lying above the curve. The calculations made by Kubo show that the thermal activation from $\mathscr{U}^g(r)$ to $\mathscr{U}^e(r)$ can occur in two different ways:

At high temperatures the activation can be treated classically. If T is the intersection point of the two curves $\mathscr{U}^g(r)$ and $\mathscr{U}^e(r)$ (see Fig. VII.1), then to obtain the escape from the trap, T must be reached

from the minimum A. This necessitates an energy E_T, which is equal to the height of the point T above A.

Actually the two curves do not cross at T but come very close to
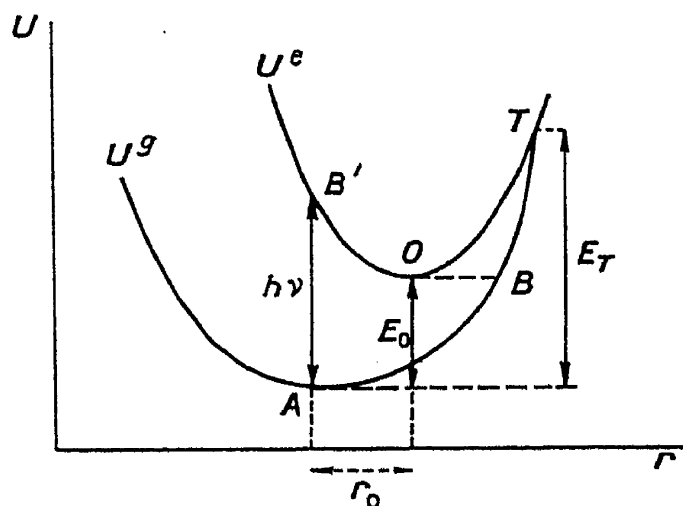
Fig. VII.1 *Escape of trapped electron described in terms of the configurational coordinate model*

E_0: *thermal activation energy for escape from trap at low temperatures*

E_T: *thermal activation energy at high temperatures*

hv: *optical activation energy*

each other. This is because two levels approaching each other produce a mutual perturbation inversely proportional to their distance apart (see Fig. VII.2). However, no difficulty is raised: the point T corre-
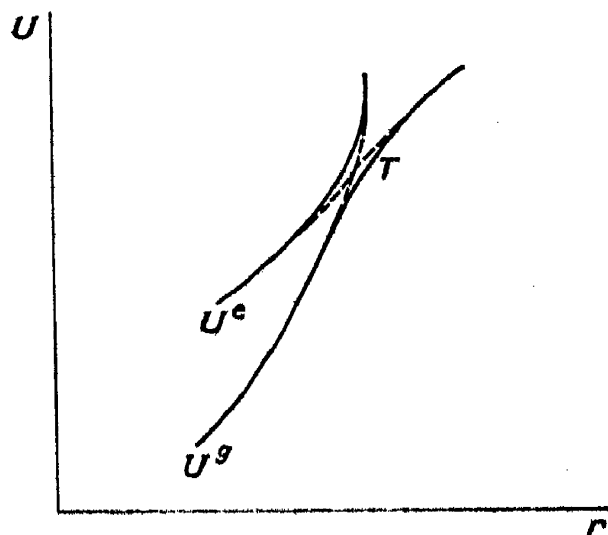
Fig. VII.2

sponds to a very high state of ionic vibration, the wave functions having amplitudes approaching the classical amplitude. Near T the transition from one curve to the other has a high probability.

If we now use the expression of Williams and Eyring for the probability p for escape from a trap, i.e.

$$p = x \nu_t \, e^{\Delta S/k} \, e^{-E_T/kT}$$

we have x little different from unity. Unless the entropy ΔS of activation is abnormally large, $p = s\, e^{-E_T/kT}$, with s only a little different from the thermal vibration frequencies, $\approx 10^{13}$ sec^{-1}, according to this mechanism.

At low temperatures activation takes place by the smallest possible energy, i.e. to B (Fig. VII.1), which has the same value at the minimum O of the curve for the excited state. Transition from B to O can then take place by a tunnel effect. The necessary activation energy is then only E_0, the height of the minimum O above A, and is smaller than that above (E_T). However, the transmission coefficient x is now small compared to unity. In this case the probability of escape is given by

$$p = s_0 \, e^{-E_0/kT}$$

with s_0 now much smaller than thermal vibration frequencies. After what has been discussed previously this would seem to be the case for ZnS, CaS and KCl(Tl), ordinary temperature being what we have called a 'low temperature' above, while the 'high temperature' conditions may apply to the traps in germanium and silicon as explored by Haynes and Lax.

2. Optical activation energies

According to the Franck–Condon principle the escape from a trap is effected by absorption of a quantum $h\nu$ equal in energy to the vertical distance AB' of the curves in Fig. VII.1. If the level $\Psi^e(r)$ is localized, there will be an absorption band in the spectrum at frequency ν. If this level is, however, the bottom of the conduction band, then absorption will occur for all frequencies greater than ν, hence a wide band with a threshold around the value ν.

$h\nu$ is the optical ionization energy of the trap while E_0 (or E_T) is the *thermal activation energy*.

If the two curves of Fig. VII.1 have a relative displacement r_0, then $h\nu > E_0$. It follows that in an *ionic crystal* the optical activation is, as a general rule, greater than the thermal activation energy E_0 (low temperature value). In some cases r_0 is very small and the difference $h\nu - E_0$ is very small. The displacement r_0 is most significant in ionic crystals as seen for KCl(Tl) (page 38) and it follows for mainly

electrostatic reasons. Overlap of ions is greater in the excited state. For a trap treated in terms of a hydrogenlike model the same applies (cf. page 166). The thermal activation E_0 occurs with removal of the
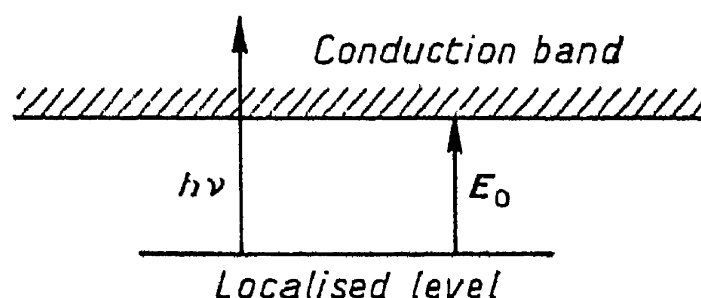
Fig. VII.3 *Thermal ionization energy E_0 and optical energy $h\nu$ in an ionic crystal*

ionic polarization due to the trapped electron, but in optical activation the polarization does not have time to disappear and the energy $h\nu - E_0$ is not recovered until later.†

In a covalent crystal the displacement r_0 is really small if not zero. In this case the optical activation process is to the minimum O of $\mathcal{U}^{\bullet}$
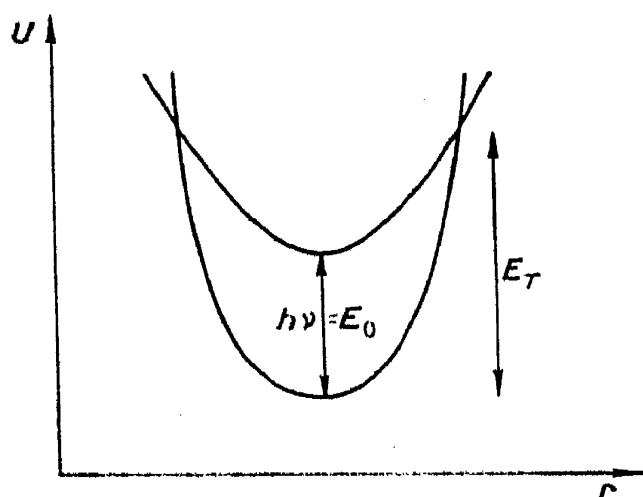
Fig. VII.4 *Case of zero displacement between configurational coordinate curves. Thermal activation energy E_0 is the same as optical activation energy $h\nu$*

and $h\nu = E_0$. In contrast we cannot compare $h\nu$ and the 'high temperature' thermal activation energy E_T, and it is easily seen that configurational curves can be drawn so that E_T can be smaller or greater than $h\nu$.

Experimentally it is very difficult to relate a particular observed optical absorption band with a particular thermal activation energy

† Except in this chapter, where we make a distinction between E_0 and E_T, we simply denote the thermal activation energy by E, which is obtained in experiment.

for trapped electrons, and this is especially so when there is ionization of the trapped electrons without an intermediate excited level transition. In this case ν gives the threshold of the band and not its maximum.

We give here some examples:

(i) For F centres in KCl, if the thermal glow peak at 620°K is due to emptying of F centres, then

$$h\nu = 2 \cdot 3 \text{ eV}; \qquad E_0 = 1 \cdot 8 \text{ eV}$$

(ii) For the metastable state $^3P_0$ of thallium in KCl, for which $E_0 = 0 \cdot 67$ eV, the optical activation energy is approximately given by a stimulation band at $1 \cdot 15 \, \mu$ ($1 \cdot 07$ eV) according to data from Johnson and Williams. If the explanation of this band is correct, then

$$h\nu = 1 \cdot 07 \text{ eV}; \qquad E_0 = 0 \cdot 67 \text{ eV}$$

The energy is that required to raise the Tl^+ ion from the trapping state to the excited state $^3P_1$. With an energy of 4 to 5 eV (2,500 Å excitation), the trapped electrons may be liberated into the conduction band of the KCl crystal. Experimentally, F centres are then found which indicates a transit of electrons through the conduction band.

(iii) In ZnS(Ag) phosphors Lambe and Klick have shown the existence at liquid air temperature of a stimulation band at $2 \cdot 6 \, \mu$ ($0 \cdot 47$ eV). It is tempting to suggest a correlation between this band and the most important groups of traps with $E = 0 \cdot 28$ eV, i.e.

$$h\nu = 0 \cdot 47 \text{ eV}; \qquad E_0 = 0 \cdot 28 \text{ eV}$$

However, no stimulation band is found to correlate with the groups at $0 \cdot 50$, $0 \cdot 57$, $0 \cdot 65$ and $0 \cdot 72$ eV, &c., which occur in ZnS(Cu). What is observed is a broad stimulation band in the infra red at about $1 \cdot 3 \, \mu$ ($0 \cdot 96$ eV). The difference between the optical and thermal depths has the right sign, however, the photon activation of the trapped electrons is not likely to be the result of a direct photon absorption in the traps but rather of an absorption transition involving other levels in the phosphor, followed by an energy transfer. This problem is still under discussion.

(iv) In germanium, which is not an ionic crystal, the optical and thermal activation energies of donor levels (hydrogenlike) are very close in value. They are a little less so in silicon. Picus, Burstein and Henvis give for impurities P, As and Sb in silicon:

	P	As	Sb
E_0 (eV)	0·045	0·049	0·039
$h\nu$ (eV)	0·050	0·053	0·042

(v) Urbach cites a case where the difference is small, although it involves an ionic crystal (perhaps r_0 is very small). In the highly stimulable phosphors SrS(Eu, Sm) the infra-red stimulation is sensitized by Sm, giving a band with a maximum at $1 \cdot 02 \mu$ ($1 \cdot 2$ eV), which also gives a deep trap having a glow peak at 650°K. This corresponds to a thermal activation energy of about $1 \cdot 2$ eV, the experimental accuracy not being great enough to establish the exact identity between the two values or in which sense the difference might exist.

3. Description of effects shown by the highly stimulable alkaline earth sulphides (containing two activator impurities)

The sulphides concerned are of the type

$$\text{SrS(Eu, Sm)}; \qquad \text{SrS(Ce, Sm)}$$

The host material can be CaS, SrSe, &c. Europium or cerium can be replaced by manganese or copper while samarium may be replaced by bismuth.

The usual emission under ultra-violet excitation is the green for cerium, yellow for manganese and orange-red for europium, these being known as the *principal or dominant activators*. The *secondary activator* samarium gives an orange-red band which is thus usually obscured by the emission of the first activator.

The effects are particularly striking in the case of SrS(Ce, Sm) because of the marked difference in colour of the emissions of the two activators. We shall describe them in some detail.

The green emission shows little persistence and during the decay a feeble orange-red emission is also seen. As in decay, the thermoluminescence is green for the shallower traps and orange-red for the deep traps, i.e. at higher temperatures; this indicates that the deep traps are introduced by the samarium.

The stimulability of the phosphor is due to the samarium, which is thus called a *sensitizer*. It is shown by stimulation spectra (see Fig. VII.5) that the spectrum is characteristic of samarium and independent of the particular dominant activator.

The stimulation spectrum is the curve which shows the maximum value reached by the emission intensity I_λ during the stimulation process as a function of the wavelength (λ) of the stimulating infra-red radiation. However, the colour of the stimulated emission is characteristic of the principal activator. The green cerium emission again

masks the orange-red emission of the samarium. The effect has military applications (infra-red signalling and image converters). For this the SrS(Eu, Sm) phosphor is used because the green emission of SrS(Ce, Sm) is too easily seen at a distance.

The transitions responsible for the light emission from the activators are probably most conveniently described as occurring between levels of the activator ions. This is at least true for the ground state. The excited level is very shallow with respect to the conduction band. The luminescence processes in these phosphors are accompanied by photoconduction phenomena and the centres are ionized (Keller and Pettit).

The unexcited cerium and samarium ions occur in the phosphor as
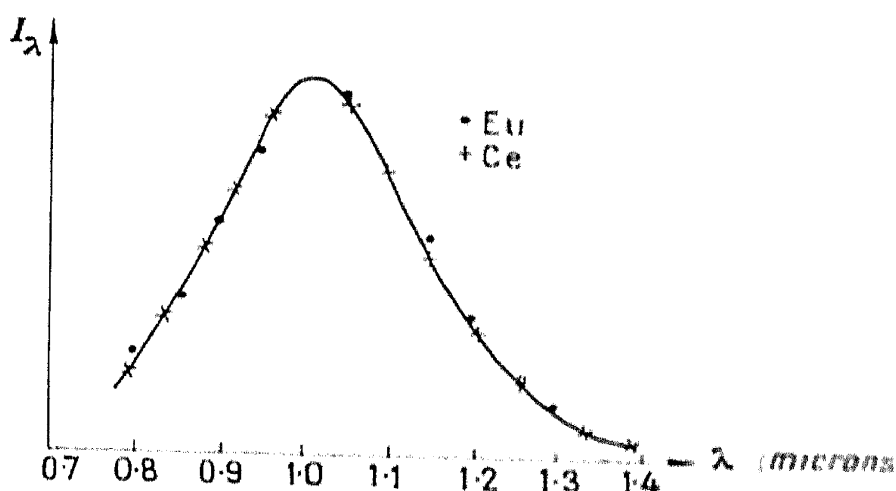
Fig. VII.5 *Stimulation spectra of SrS(Eu, Sm) and SrS(Ce, Sm)*
(After B. O'Brien)

Ce^{3+} and Sm^{3+} which is the usual valency state for rare earths. The neutral cerium atom has the following electronic configuration:

$$Ce: \ldots 4f^1\ 5s^2\ 5p^6\ 5d^1\ 6s^2$$
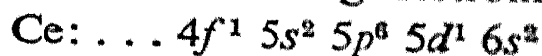
and the trivalent ion:

$$Ce^{3+}: \ldots 4f^1\ 5s^2\ 5p^6$$
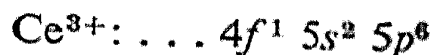
The fundamental state of Ce^{3+} is the doublet ${}^2F_{5/2}$, ${}^2F_{7/2}$, whose separation is about 0·20 eV (Kröger and Bakker). This doublet leads to a double-peaked emission spectrum.†

On the other hand, the europium atom, which is the sixth in the rare earth series, might have the configuration:

$$Eu: \ldots 4f^6\ 5s^2\ 5p^6\ 5d^1\ 6s^2$$
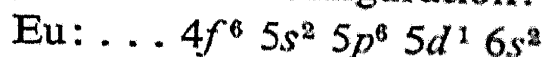
† The crystal field splitting of the levels is probably smaller.

but in fact the stability is higher if the $4f$ shell is half-filled with 7 electrons and the internal ion is thus divalent:

$$\text{Eu}^{3+}: \ldots 4f^6 \ldots \text{(basic level } {}^7F_0)$$
$$\text{Eu}^{2+}: \ldots 4f^7 \ldots \text{(basic level } {}^8S_{7/2})$$

Paramagnetic resonance experiments show that indeed in the SrS phosphors cerium occurs as Ce^{3+} and europium as Eu^{2+} (W. Low). Experiments by Antonov-Romanovsky, Dubinin and Trapeznikova support the conclusion that the Eu^{2+} ions are ionized during the excitation. For Eu^{2+} the observation of paramagnetic resonance absorption can be made at room temperature since the relaxation times in an S-state are rather large, while Ce^{3+} and Sm^{3+} give paramagnetic resonance only at low temperatures and Eu^{3+} is in the non-paramagnetic state ${}^7F_0$. As a result a decay of the intensity of the room
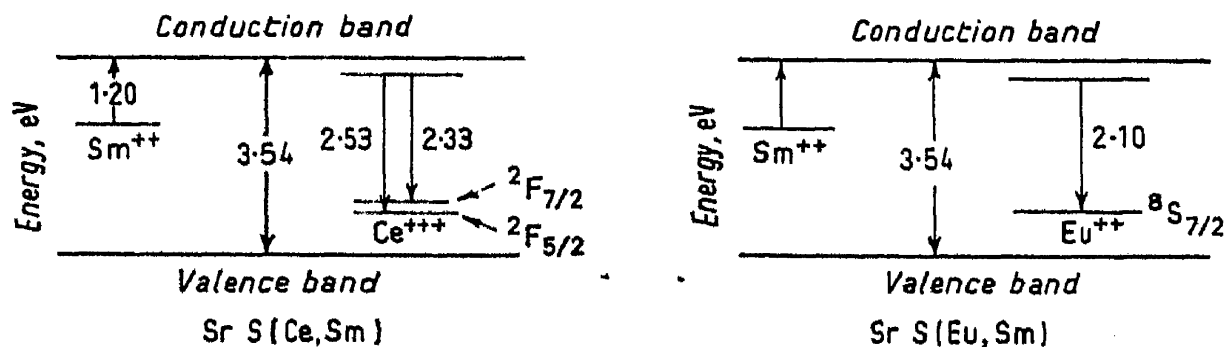
Fig. VII.6 *Models for luminescence emission and infra-red stimulation in SrS(Ce, Sm) and SrS(Eu, Sm)*
(*From Keller, Mapes and Cheroff*)

temperature paramagnetic resonance absorption is observed when the phosphor SrS(Eu, Sm) is excited by ultra-violet radiation.

The nature of the samarium trapping states is less well known. But we might accept the hypothesis of Keller, Mapes and Cheroff describing it as a Sm^{3+} ion which has captured an electron

$$(\text{Sm}^{3+} \longrightarrow \text{Sm}^{2+})$$

According to these authors, the 1-micron infra-red absorption leads to the ionization of the Sm trap and ejection of the electron into the conduction band followed by light emission from the activator ions. No perturbing or quenching phenomena occur under irradiation at this wavelength. The interpretation of stimulation effects has raised several problems which are in sight of solutions.

While samarium gives rise to the same stimulation band in both SrS(Ce, Sm) and SrS(Eu, Sm) with a maximum at $1 \cdot 02 \ \mu$, the

thermoluminescence peak observed at 650° K for the sulphide acti-
vated by europium is not observed for that activated by cerium.
Instead, a shallower trap occurs, giving a peak at 420°K.

We might ask whether there is any connection between the 'optical
traps' (Sm levels) responsible for stimulation and the 'thermal traps'
(levels responsible for the thermal glow peaks). It is simpler to assume
that in both SrS(Ce, Sm) and SrS(Eu, Sm) phosphors the metastable
level due to Sm is the same but that thermal quenching masks the
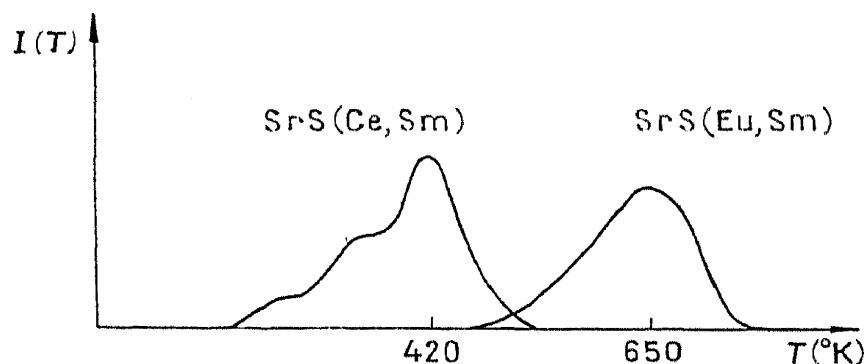
Fig. VII.7 *Thermoluminescence curves of SrS(Eu, Sm)
and SrS(Ce, Sm) phosphors
(After F. Urbach)*

thermoluminescence peak at 650°K in the first case but not in the
second.

The ground state of Eu^{3+} will be above the valence band at a height
near to that for Ce^{3+}, but the ground state of Eu^{2+} will be somewhat
higher. Thus a large activation energy will be required for freeing of
holes in SrS(Eu, Sm) than in SrS(Ce, Sm) and so thermal quenching
(as shown below) will not occur until higher temperatures are reached
in the former case.

4. Stimulation and quenching spectra of zinc and cadmium sulphides

The stimulation efficiency of ZnS(Cu) at room temperature is rather
poor. However, evidence for the occurrence of a *stimulation flash*
when an excited phosphor is submitted to an infra-red irradiation has
been given as early as in Lenard's work. The maximum of the
stimulation spectrum is situated at 1·3 μ. Another stimulation band
(0·6–0·8 μ) occurs at shorter wavelengths and adjoins the excitation
region.

The 1·3-μ band is correlated with the optical activation of the
0·5–0·8-eV traps, which are connected with the green centres (see

page 155). The green emission is thus stimulated but not the blue one (Garlick and Browne). The absence of structure in this band is in marked contrast with the structure of the trap distribution, which is revealed by the glow curves and the decay curves.

The 0·6–0·8-μ band is ascribed to the emptying of donor levels deeper than the traps.

At liquid air temperature the stimulation is stronger. To the 1·3-μ band is then added a second peak in the stimulation spectrum, at 1·2 μ (Garlick and Mason). In addition, a long-wave band now occurs at 2·6 μ and is correlated with the activation of electrons from shallow levels. The emptying of shallow traps is much easier than the emptying of deep traps.

Apart from the 1·3-μ peak, the stimulation spectra for both blue and green emission are identical (Garlick and Browne).

Fig. VII.8 *Stimulation spectrum of ZnS(Cu, Pb) at room temperature*
The same bands are observed in ZnS(Cu), without Pb, but their intensity is 10 to 20 times smaller

In sulphide phosphors, *infra-red quenching phenomena* occur also; they are competitive with the stimulation process. The quenching is most easily studied when the infra-red is applied during the ultra-violet excitation (Fig. VII.14), while the stimulation is better observed during the phosphorescence decay, i.e. when a long time – often several hours – elapses between the end of the excitation and the infra-red irradiation.

The same 1·3- and 0·6–0·8-μ radiations that are specifically active in stimulation produce also the maximum quenching effects,[†] but the quenching is equally well observed for the blue band and the green band. It is ascribed to the obstruction of the copper centres by an electron coming from the sulphur levels in the valence band (see

[†] According to G. Meijer, these bands coincide also with the excitation bands for the infra-red emission.

below, Fig. VII.13). In the case of the 1·3-μ irradiation this transition needs a thermal activation of about 0·4 eV (Broser and Broser-Warminsky, Bube and Tutihasi). The quenching is more pronounced at 290°K than at liquid air temperature.

The interpretation of this thermal activation can be looked for in a two-step excitation process. First of all the 1·3-μ infra-red photon raises a valence band electron into a metastable sulphur level S*. Then, starting from this configuration, a thermal transition obstructs the luminescence centre.

This hypothetical metastable level was first introduced to explain the two-stage extinction effects of infra-red light and electric fields on the Gudden and Pohl phenomenon (M. Curie, 1946). In modern language, the optical activation leading to this level can be described as an intra-band transition inside the valence band (see page 83).

In competition with the quenching process an energy transfer may also occur from the S* level to any of the traps. In this case the stimulation flash is produced. Thus the mechanism which is proposed here leads to an explanation of the similarity between the quenching and stimulation spectra.

Lewchin and Orlov and Garlick and Mason have shown that if the stimulation experiment is performed at various temperatures T after an excitation at a given temperature T_0, the intensity of the flash increases with T:

$$I = I_0 \, e^{-E/kT}$$

The release of electrons from traps, possibly the occurrence of the above transfer, needs thus a preliminary thermal activation. The activation energy E depends on the nature of the trap and is independent of the wavelength of the stimulating radiation (Lewchin and Orlov).

Similar phenomena occur in cadmium sulphide phosphors. However, the stimulation and quenching bands are slightly displaced towards larger wavelengths.

TABLE VII.1

	Peak position in ZnS	*Peak position in CdS*
The short wavelength stimulation band	0·75 μ	0·80 μ
The deep trap stimulation and quenching band	1·3 μ	1·4 μ
The Lambe and Klick stimulation band	2·6 μ	2·8 μ

ZnS(Cu, Pb) sensitized for infra-red radiation. G. Fonda has shown that the incorporation of Pb in a ZnS(Cu) phosphor leads to a strong enhancement of its infra-red stimulability.

At first sight one might think that lead, in the same way as samarium in the preceding paragraph, is correlated with a deep trapping level; the optical activation of this level by the infra-red photon, followed by light emission from the centres, would give an explanation of the stimulability.

However, this idea must be rejected because the stimulation spectra of ZnS(Cu) and ZnS(Cu, Pb) have the same shape (G. Curie). On
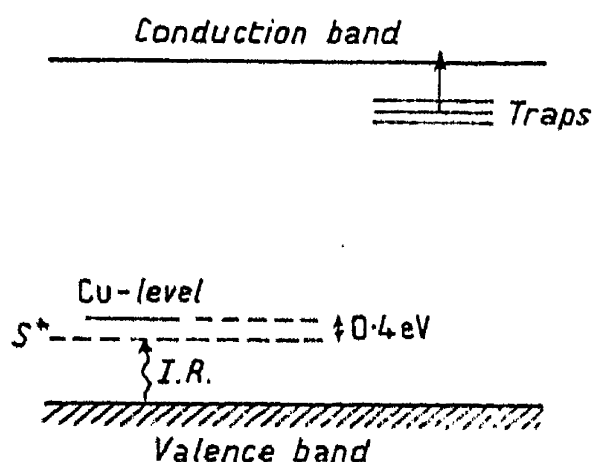
Fig. VII.9 *Proposed level scheme for the stimulation and quenching phenomena in ZnS(Cu) and ZnS(Cu, Pb) phosphors*

The $1 \cdot 3$-μ radiation raises the valence band electrons to a metastable sulphur level S^*; starting from this configuration, an energy transfer to the traps can occur (stimulation), or a thermal activation blocking access to the centre (quenching).

In addition, in a ZnS(Cu, Pb) phosphor the free holes in the valence band are trapped in the Pb centres, whence an increased probability of light emission occurs

(H. Kallmann)

the contrary, the shape of the stimulation spectrum of a samarium-sensitized sulphide is characteristic of the nature of the sensitizer. In ZnS(Cu, Pb) the stimulation *intensity* (height of the spectrum) is merely increased by the addition of lead.

Thus in ZnS(Cu, Pb) the absorption of the infra-red photons most likely involves the same transition as in ZnS(Cu), i.e. an intra-band activation to the S^*-level, followed by an energy transfer to the traps.

This mechanism does not depend on the incorporation of Pb. The stimulating action of this activator is then simply ascribed to a large cross-section for electron-hole radiative recombination in the lead centre (H. Kallmann).

The emission due to the lead activator is in the green region of the visible spectrum as for the main band of copper, but spectral distribution measurements show differences. The maximum of the Pb band is situated at $0.51\ \mu$, while that of the Cu band peaks at $0.523\ \mu$. During the stimulation of emission the spectrum of Pb only is observed (G. Fonda, V. L. Lewchin).

II. NON-RADIATIVE CAPTURE BY IMPURITY-STATES, THERMAL AND OPTICAL QUENCHING OF LUMINESCENCE

1. Non-radiative capture by traps

The non-radiative capture of an electron by a trap, with dissipation of the excess energy as phonons and not as photons, can be described using Fig. VII.1 by a process inverse to that of thermal activation. An electron initially in the excited state $\mathcal{U}^e$ falls to the ground state $\mathcal{U}^g$ with the emission of vibrational quanta in the crystal lattice. At high temperatures this transition necessitates a thermal activation energy E^* from the minimum O of the excited state to the neighbourhood of T where the transition between the curves for the two states $\mathcal{U}^g$ and $\mathcal{U}^e$ is highly probable. We thus obtain a probability for the non-radiative transition or capture: $P_{cap.} = s\,e^{-E^*/kT}$, where $E^* = E_T - E_0$. This is the classical approach first described by Mott.

At lower temperatures, non-radiative capture involves a transition from the one state $\mathcal{U}^e$ to the other $\mathcal{U}^g$ by tunnelling at the height of the minimum O.

$$P_{cap.} = \text{quasi-constant.}$$

In both cases the ratio of the probabilities $P_{cap.}$ and $P_{(escape)}$ will be given by the same exponential factor

$$\frac{P}{P_{cap.}} \propto e^{-E_0/kT}$$

Thus it is the thermal ionization energy for low temperatures (E_0) which is involved in applying the law of detailed balancing (see Chapter VI, §I.4).

2. Thermal quenching of luminescence

The intensity of luminescence during excitation falls if the temperature is raised sufficiently; emission of lattice vibrations occurs in competition with the photon emission.

If P_r is the probability of luminescence emission and P_{nr} the probability of a non-radiative transition, then the luminescence is proportional to the ratio

$$\eta = \frac{P_r}{P_r + P_{nr}}$$

which is called the luminescence efficiency. It is assumed that P_r is sensibly independent of temperature, while P_{nr} rises rapidly with temperature.

(*A*) *Thermal quenching according to the theory of Mott and Seitz.* This is applicable when the radiative and non-radiative transitions compete within the confines of the luminescence centres; this is the case for KCl(Tl). If we look again at the configurational coordinate curves
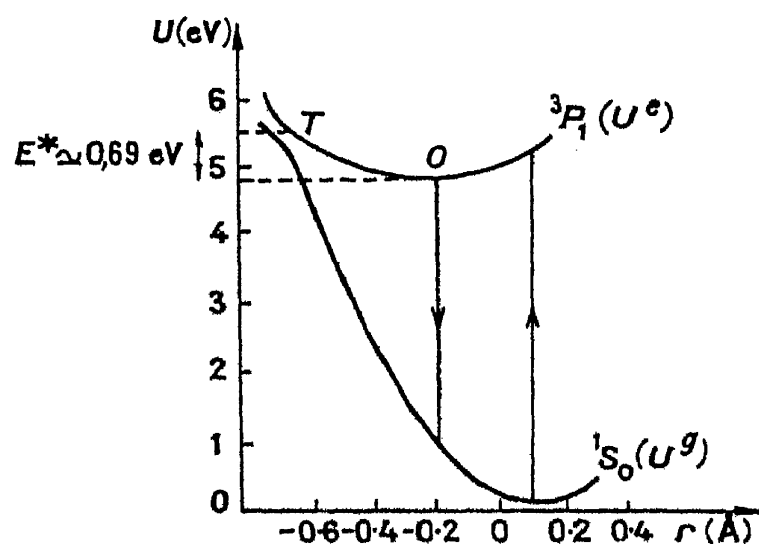
Fig. VII.10 *Mechanism for non-radiative transitions in the configurational coordinate theory (Mott)*

of Fig. II.5, obtained by F. E. Williams to account for the absorption and emission bands, we can produce them until they reach their 'intersection' T (see Fig. VII.8). At low temperatures there may be some non-radiative transitions, but they will only become important about 500°K where quenching occurs. The efficiency is well represented by

$$\eta = \frac{1}{1 + C\,e^{-E^*/kT}}, \quad \text{where } C \text{ is a constant.}$$

The experimental activation energy $E^* \approx 0.60$ eV is in good

agreement with the value of 0·69 eV obtained by extrapolating the configurational coordinate curves.

This model will apply when the minimum O of the excited state falls within the limits of the ground state curve $\mathcal{U}^g$. This gives a lumi-
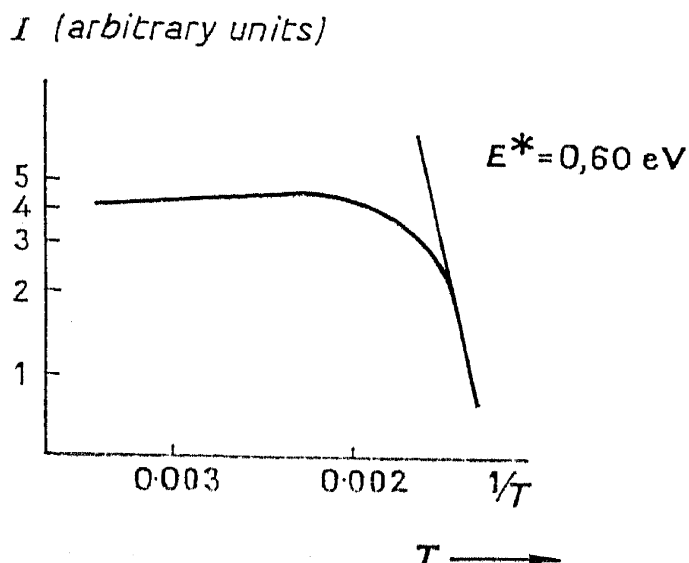
Fig. VII.11 *Efficiency of 3,050 Å emission of KCl(Tl) as a function of temperature (Johnson and Williams)*

nescent solid at low enough temperatures with quenching at higher temperatures and is the case considered by Mott.

If in contrast to this the minimum O lies outside the ground state curve it corresponds to a metastable state from which a luminescence transition is not possible. The 'de-excitation' occurs by a thermal activation OT (see Fig. VII.12) followed by phonon emission as the only possible transition so that the material is non-luminescent. We
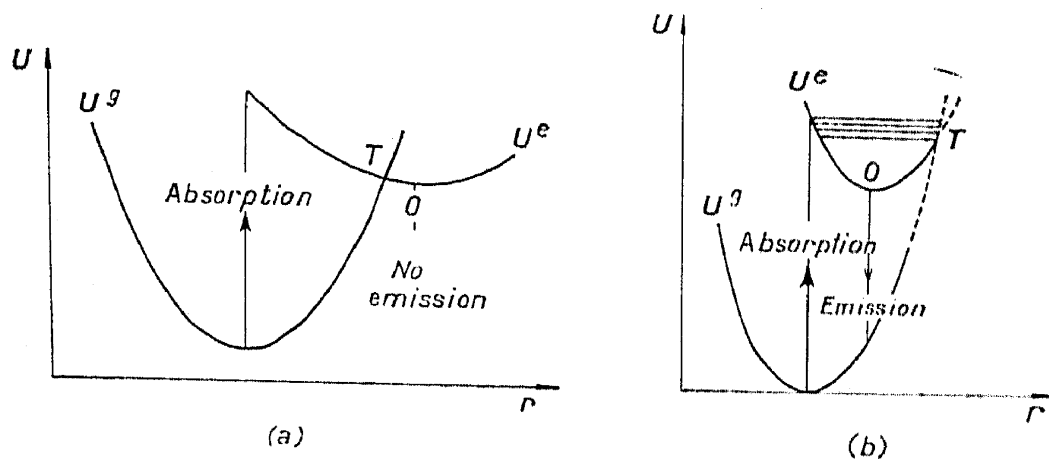
Fig. VII.12 *Two arrangements of configurational co-ordinate curves:*

(a) (*Seitz*) *for a non-luminescent solid*

(b) (*Dexter, Klick and Russell*) *a luminescent solid, but one with a high probability for non-radiative transitions*

do not know if this applies to an actual solid; in any case it is necessary to assume a very large displacement between the excited state and the ground state equilibrium positions.

Returning to the arrangement of curves assumed by Mott, Dexter, Klick and Russell have observed that if absorption leads to a transition from $\mathscr{U}^g$ to a point high up on $\mathscr{U}^e$ and near in energy to the inter-section T, then in order to reach O from which the lumniescence transition occurs, the crystal has a large chance of passing through the configuration corresponding to the point T. No activation energy is needed in this case to reach T and so a low emission probability will result even at low temperatures.

The conditions for this arrangement to occur are easily seen to obtain when the vibrational frequencies for the centre are the same in the ground and excited states. There must then be between the mean absorption and emission frequencies the following relation:

$$h\nu_{0 \text{ (emission)}} \approx \tfrac{1}{2}h\nu_{0 \text{ (absorption)}}$$

As a general observation we see that a large displacement between ground and excited states (giving a marked Stokes's law effect) will involve a high probability of non-radiative transitions (i.e. poor luminescence efficiency).

(B) *Thermal quenching in phosphorescent sulphides.* The first theory of thermal quenching in phosphorescent photoconductors introduced the direct non-radiative recombination between conduction-band electrons and holes in the valence band (Möglich and Rompe, 1940). If the probability for phonon emission is of the form $a(\bar{n}+1)$, then

$$\bar{n} = \frac{1}{e^{\hbar\omega/kT}-1}$$

where $\bar{n}$ is the mean number of phonons present at the particular temperature. The probability of simultaneous emission of g phonons is proportional to the product

$$P_{nr} \propto \prod_g (\bar{n}+1)$$

Now $g = \dfrac{E_{\text{gap}}}{\hbar\omega}$ and is of the order of 50–100 in CdS and 100 to 150 in ZnS. At temperatures at which spontaneous emission is negligible

$$P_{nr} \propto \left(\frac{kT}{\hbar\omega}\right)^g$$

$$\eta = \frac{1}{1+CT^g}$$

Experiment shows that an expression of this form is in good agreement with experiment, but $g \approx 10$ instead of 50 to 100 (Peyrou). It would seem that non-radiative transitions of the Möglich and Rompe type will only occur at relatively high temperatures ($\approx 1,000°K$), while at temperatures where the efficiency is low (300° to 500°K) they will occur via defects (Rompe, 1952).

The generally accepted Schön–Klasens scheme of Fig. VII.13 furnishes a simple and interesting explanation of thermal quenching in the sulphides.

An electron in the valence band can enter a luminescence centre by a thermal activation of energy W. The electron previously removed from the centre by excitation cannot now return and after diffusing in the conduction band for a while will finally recombine via some
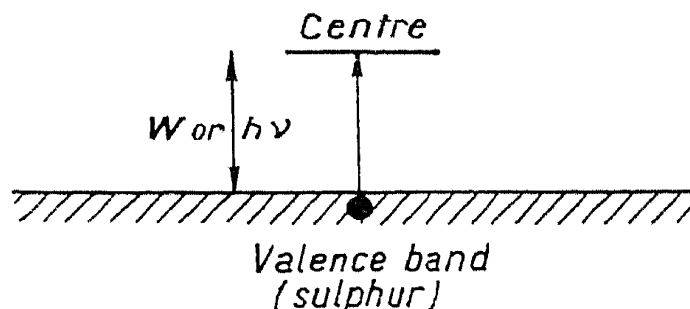
Fig. VII.13 *Schön–Klasens model for thermal quenching of luminescence in sulphide phosphors*

defect or other (eventually in a killer centre such as iron, nickel or cobalt if these are present).

If there are a sufficient number of defects available the thermal activation process will determine the probability of quenching and we have

$$\eta = \frac{1}{1 + C\,e^{-W/kT}}$$

being of the same form as in the theory of Mott and Seitz, but with a different interpretation placed on the energy W.

The same transition W can occur by absorption of an optical photon $h\nu$: this explains the quenching effect of infra-red radiations (see page 199). This phenomenon may be considered as photon absorption effect in the sulphur atoms (M. Curie, 1923), leading to a filling of the centres. This description in terms of the energy band scheme was first given by P. Brauer.

This quenching (see Fig. VII.14) may occur either by one optical

transition only (0·6–0·8-μ band in ZnS) or by a two-step process needing a thermal activation (1·3-μ band in ZnS).

Discussion of the various models. The idea which ascribes both thermal and optical quenching to the same kind of transitions looks rather
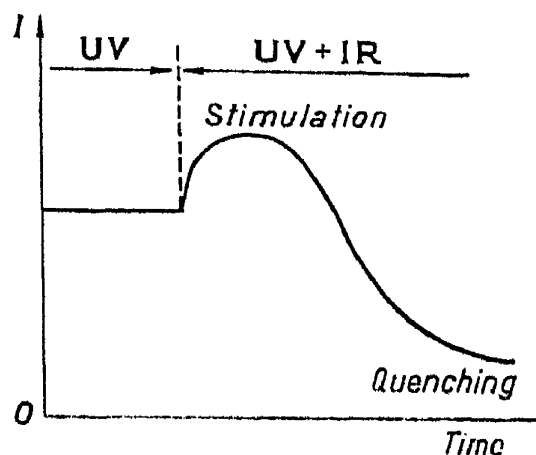

Fig. VII.14 *Luminescence under constant excitation. Effect of infra-red stimulation followed by permanent quenching effect*

tempting. Unfortunately, it does not seem to be supported by experimental evidence.

The similarity of the infra-red extinction spectra for both blue and green emission bands in ZnS (Garlick and Browne) is in marked contrast to the observed difference between their respective thermal extinctions: it is well known that thermal quenching occurs about 150° higher for the green band than for the blue band.†
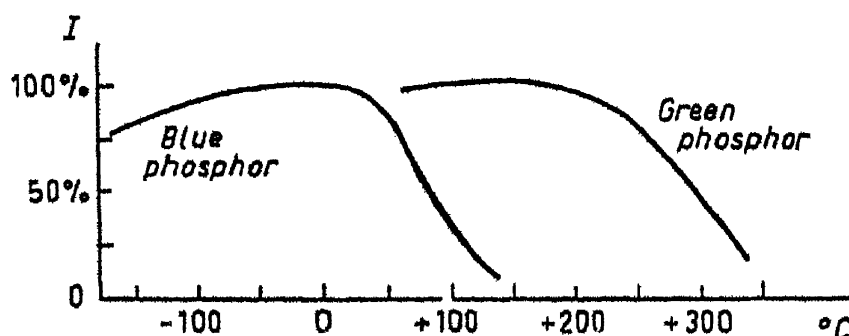
Fig. VII.15 *Temperature dependence of the luminescence of a ZnS(Cu) phosphor for excitation by 3,650 Å radiation*
(*F. A. Kröger*)

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† For instance, the fall in the luminescence intensity begins near 0°C for the blue band of a given phosphor, and near 150°C for the green band. However, large differences are found between these values for different samples: this fact proves that the non-radiative electron-hole recombinations occur in the defects of the crystal and not by band-to-band recombinations.

In the present state of affairs, if we accept the above mechanism for the infra-red activation, we must place the blue and green emitting copper centres at the same height above the valence band, while if we accept the Schön–Klasens mechanism for the thermal quenching, we

Conduction band

$\uparrow W$

Excited associated level

Fundamental copper level

$h\nu \uparrow$

Valence band
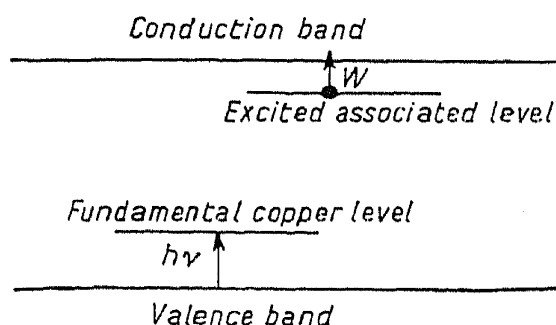
Fig. VII.16 *Thermal and optical quenching according to the model for centres proposed in Fig. V.5*

Optical quenching is assumed to occur according to Brauer's and Schön–Klasen's model while thermal quenching occurs when the thermal activation W happens before the light-emitting transition (Roberts and Williams).

We emphasize that, of course, at sufficiently high temperatures the filling of the ground state by thermal activation also occurs

have to place the green level higher than the blue one (see Chapter V, Figs. V.3 and V.5). Further studies are needed in order to choose between these different models. Electroluminescence studies support the assumption of the same ground state occurring in both centres, i.e. Fig. V.5.

III. THE THEORY OF MULTIPHONON TRANSITIONS

We denote by *multiphonon transitions* the simultaneous absorption or emission of a large number of thermal vibration quanta. These transitions have been much investigated by theoreticians over the last decade. The author believes that the 'common sense' view of progressive activation or de-activation via defects (see page 144) corresponds more closely to reality. Nevertheless, these theories of multiphonon transitions, apart from their intrinsic interest, offer a chance of clarifying the ideas discussed above.

We use the same notation as in section III.4 of chapter II. Consider the transition (by thermal activation) between the ground state $\mathscr{U}^g$ in which the vibration of the ions is characterized by a quantum num-

ber m and the excited state in which the vibrational state is n. The quantum then is assumed to be the same in the ground and excited states.

The transition takes place with absorption of $p = m - n$ quanta. We introduce an absorption operator (phonon annihilation)

$$a\psi_m = \sqrt{m}\,\psi_{m-1}$$

and an emission operator (phonon creation)

$$a^*\psi_m = \sqrt{m+1}\,\psi_{m+1}$$

The matrix element relative to the operator a is

$$\int \psi_n(r - r_0)a\psi_m(r)\,\mathrm{d}r = \sqrt{m}\int \psi_n(r - r_0)\psi_{m-1}(r)\,\mathrm{d}r$$

$$= \sqrt{m}\Lambda_n{}^{p-1}(S)$$

Λ being a normal Laguerre function of the configurational parameter S. The matrix element of the operator a^* is $\sqrt{m+1}\Lambda_n{}^{p+1}(S)$. When S is zero, i.e. no displacement r_0 between the two oscillators $\mathscr{U}^g$ and $\mathscr{U}^e$, the only non-zero $\Lambda_n{}^p$ is that for $p = 0$. Thus the matrix element of the operator a is only different for $p = 1$ (absorption of a quantum) and that for a^* only for $p = -1$ (emission of a quantum).
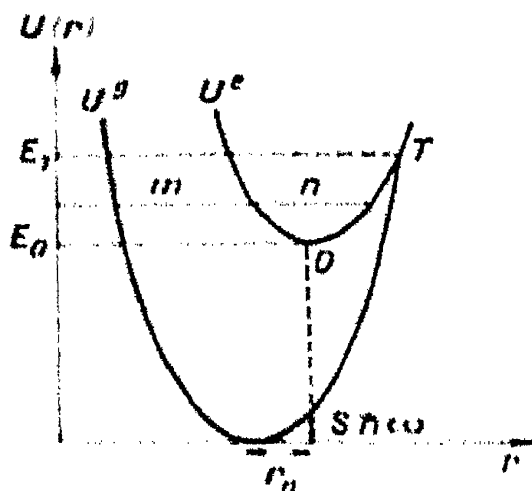
Fig. VII.17 *Thermal activation and non-radiative capture by an impurity level: transition from a vibrational level m to vibrational level n*

However, when S is not zero all the Λ's are different from zero. Thus the operators a and a^* permit both absorption and emission of a number of phonons p when the oscillators $\mathscr{U}^g$ and $\mathscr{U}^e$ are displaced relative to each other ($r_0 \neq 0$). The greater the Stokes's shift, $2S\hbar\omega$,

between emission and absorption of radiation, the greater the chance of non-radiative transitions.†

The transition probability due to the operator a is

$$p_a = \sum_{\substack{m=p \\ n=0}}^{\infty} m \, | \, \Lambda_n{}^{p-1}(S) \, |^2 \, \frac{\mathrm{e}^{-m\alpha}}{\sum_0^{\infty} \mathrm{e}^{-m\alpha}}$$

where $\alpha = \hbar\omega/kT$. The summation is made by use of the Myller–Lebedeff formula. We obtain

$$p_a = p\frac{\mathrm{e}^{\alpha/2}}{\mathrm{e}^{\alpha}-1} \, \mathrm{e}^{-p\alpha/2} \, \mathrm{e}^{-S\cot(\alpha/2)} \, I_{p-1}\!\left(\frac{S}{\sinh(\alpha/2)}\right)$$

by neglecting the terms linear in S (S small). If $\bar{n} = \dfrac{1}{\mathrm{e}^{\alpha}-1}$ is the mean number of phonons present at T:

$$p_a = p\sqrt{\bar{n}(\bar{n}+1)}\left[\frac{\bar{n}+1}{\bar{n}}\right]^{-p/2} \exp\left[-S(2\bar{n}+1)\right]I_{p-1}[2S\sqrt{\bar{n}(\bar{n}+1)}]$$

The transition probability due to the operator a^* is similarly

$$p_{a^*} = p\sqrt{\bar{n}(\bar{n}+1)}\left[\frac{\bar{n}+1}{\bar{n}}\right]^{p/2} \exp\left[-S(2\bar{n}+1)\right]I_{p+1}[2S\sqrt{\bar{n}(\bar{n}+1)}]$$

The adiabatic approximation for the movement of the ions shows that the actual operator to consider is not a but $(a-a^*)/\sqrt{2}$. If S is small the contribution of a to the thermal activation probability p will be sufficiently large compared with that of a^* for the latter to be neglected. We can thus assume $p \approx p_a$ and similarly the non-radiative capture probability $p_{\text{cap.}} \approx p_{a^*}$.

These formulae are due to Huang and Rhys, Pekar and Krivoglaz, Vasileff, Kubo and Toyozawa, &c.

Using the asymptotic forms for I_p, we obtain at low temperatures
$$p_a \propto \exp\left(-p\hbar\omega/kT\right)$$
$$p_{a^*} \propto \text{quasi-constant}$$
while at high temperatures
$$p_a \propto \exp\left[-\hbar\omega(p+S)^2/4SkT\right]$$
$$p_{a^*} \propto \exp\left[-\hbar\omega(p-S)^2/4SkT\right]$$

† We must emphasize that no discrepancy exists between this assertion, which takes into account the case of different centres with different values of r_0, and 'Vavilov's law' – as corrected by Louchtchik for solid crystal phosphors – which states that the luminescence efficiency is a steplike function of the wavelength of the exciting radiation; it is a constant when the exciting radiation is changed, but remains within the same absorption band of a given centre. See page 49 for the case of KCl(Tl) and page 227 for the case of ZnS phosphors.

The activation energies in three of these equations can be identified with E_0, E_T and $E^* = E_T - E_0$ respectively in agreement with the general considerations of the preceding sections.

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Energy Transfer, Sensitization
and Concentration Quenching

Energy transfer occurring in luminescence during absorption and emission is not simply confined to the same centre. Energy transfer during fluorescence between molecules of a gas or in organic solutions has been extensively studied, but such transfer plays an important role in solids; a notable example is the phenomenon of *sensitization*.

The sensitization effect was discovered in SrS(Gd, Sm) by Tomaschek and in CaS(Sm, Bi) by Rothschild. In recent years numerous studies of the effect have been made, particularly by Botden and Kröger, Butler, Dexter and Schulman, Fonda, Froelich, Janin and Crozet, Ginther and Leach.

Take, for example, the phosphor $Ca(PO_4)_2 + Ce$ (sensitizer) $+ Mn$ (activator) investigated by Botden.

Calcium phosphate activated by manganese has a red fluorescence when excited by cathode rays, but is not excited by ultra-violet radiation (2,500 Å). The latter falls outside the characteristic absorption of the Mn^{2+} ion. Activated by cerium alone, ultra-violet excitation (2,500 Å) produces an ultra-violet fluorescence (at about 3,500 Å) due to transitions in the Ce^{3+} ion. The ground state is the doublet $^2F_{5/2}$–$^2F_{7/2}$ and the excited state is most likely derived from the $^2D_{3/2}$ and $^2D_{5/2}$ states of the Ce^{3+} ions, split by the electric field in the crystal. In $Ca(PO_4)_2(Ce, Mn)$ the absorption due to Ce^{3+} ions in the 2,500-Å region is not altered by the presence of manganese. However, 2,500-Å excitation now produces both the ultra-violet emission of the Ce^{3+} ions and the red emission of the Mn^{2+} ions. Absorption is by the Ce^{3+} ions, but is followed by transfer of energy to the Mn^{2+} ions which occurs by a resonance process.

I. RESONANCE TRANSFER BETWEEN ATOMS WITH OVERLAPPING ELECTRIC FIELDS

Resonance occurs between two configurations:

ψ_i where S is excited and A not excited (S^*A)

ψ_f where S is 'de-excited' and A excited (SA^*)†

S and A representing the sensitizer and activator centres respectively.
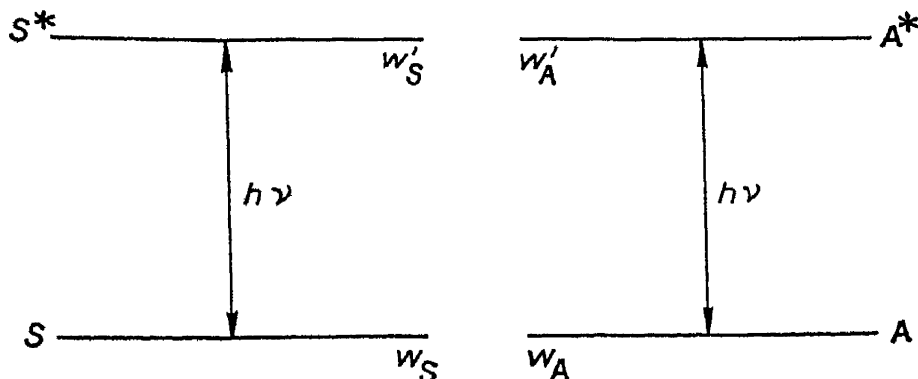
Fig. VIII.1 *Resonance transfer of energy*

S: ground state of sensitizer, S^* its excited state
A: ground state of activator, A^* its excited state
Excitation passes from S to A (S^* is 'de-excited' and A excited) without electric charge transfer between S and A

The probability of the transfer $S^* \longrightarrow A^*$ per unit time is given by

$$P_{SA} = \frac{4\pi^2}{h} \int \int \int g(w_S')g(w_A) \, | \, M \, | \, ^2 \, dw_S' \, dw_A' \, d(h\nu)$$

$g(w_S')$ and $g(w_A)$ being statistical weighting factors. The matrix element M for the transition is of the form

$$M = \int \psi_i \delta H \psi_f \, d\tau$$

where δH is the coulombic interaction between S and A, i.e. it is the same operator as that responsible for Van der Waals forces

$$\delta H = -\frac{e^2}{KR^3} \left[3\frac{(\mathbf{r}_S.\mathbf{R})(\mathbf{r}_A.\mathbf{R})}{R^2} - \mathbf{r}_S.\mathbf{r}_A \right]$$

for the dipole–dipole interaction approximation. K is the dielectric constant of the matrix medium. $\mathbf{R}$ is the distance between the nuclei of S and A, $\mathbf{r}_S$ is the distance of the electrons of S from the nucleus

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† The achievement of a configuration in which resonance is possible may involve a thermal activation energy: in this case the transfer efficiency will be temperature dependent.

of S (the sum of the distances if there are several electrons) and similarly for r_A. The matrix element M is thus given by

$$M = -\frac{1}{KR^3}\left[3\frac{(\mathbf{M}_S.\mathbf{R})(\mathbf{M}_A.\mathbf{R})}{R^2} - \mathbf{M}_S.\mathbf{M}_A\right]$$

by introducing the matrix $\mathbf{M}_S$ of the sensitizer dipole moment and that $\mathbf{M}_A$ for the activator.

$$\mathbf{M}_S = -e\int\psi_{S*}\mathbf{r}_S\psi_S\,dr_S$$

and similarly for $\mathbf{M}_A$. The mean value of M is then given by

$$|M|^2 = \frac{1}{K^2R^6}\cdot\frac{2}{3}|\mathbf{M}_S|^2.\,|\mathbf{M}_A|^2$$

and so

$$P_{SA} = \frac{4\pi^2}{h}\cdot\frac{1}{K^2R^6}$$

$$\times\frac{2}{3}\int_{h\nu}\left\{\int g(w_S')\,|\mathbf{M}_S|^2\,dw_S'\int g(w_A)\,|\mathbf{M}_A|^2\,dw_A\right\}d(h\nu)$$

There is no question of calculating these integrals; we use the emission spectrum of S^* and the absorption spectrum of A respectively as determined experimentally. It is convenient to introduce on the one hand the form of these spectra normalized to unit area $[\varepsilon_S(h\nu)$ and $\alpha_A(h\nu)]$ and on the other hand the normalization constants. If τ_S is the mean life time of S^* before emission and the effective absorption cross-section of A is σ_A, then

$$P_{SA} = \frac{3}{64\pi^5}\cdot\frac{h^4c^4}{K^2R^6}\cdot\frac{\sigma_A}{\tau_S}\int_0^\infty\frac{\varepsilon_S(h\nu)\alpha_A(h\nu)}{(h\nu)^4}\,d(h\nu)$$

We can write

$$P_{SA} = \left(\frac{R_0}{R}\right)^6\cdot\frac{1}{\tau_S}$$

where R_0 is known as the transfer distance and is interpreted as that for which

$$P_{SA} = \frac{1}{\tau_S}$$

For $R < R_0$ transfer occurs before S has a chance to be 'de-excited' by emission. In this last formula we have introduced the measured life time which is different from the life time before emission by a factor η_S.

i.e. $$\tau_{S(\text{measured})} = \eta_S.\tau_{S(\text{before emission})}$$

Thus

$$R_0{}^6 = \frac{3}{64\pi^5} \cdot \frac{h^4 c^4}{K^2} \sigma_A \eta_S \int_0^\infty \frac{\varepsilon_S(h\nu)\alpha_A(h\nu)}{(h\nu)^4} \, d(h\nu)$$

The overlap between the spectra ε_S and α_A is usually better if S and A are identical. Thus the transfer between the Ce^{3+} sensitizer and the Mn^{2+} activator in $Ca_3(PO_4)_2$ is effected by a series of transfers between cerium ions until the excitation reaches a cerium ion near to a manganese ion. Botden and Kröger reserve the term *transfer* for the basic resonance process and call the general process the energy *transport*. In the particular example above the transfer distance between two Ce^{3+} ions is estimated to be $R_0 \approx 35$ Å.

In organic solutions spectral overlap is more marked and for fluorescein ions in solution $R_0 \approx 70$ Å. We can think of associated pairs SA for which the overlap of ε_S and α_A would be better than the overlap of ε_S and α_S. It would be interesting to study the kinetics of energy transfer in such a case.

The theory of sensitization has been developed by Kallman and London, by F. Perrin, by Vavilov and that used here by Th. Förster and by Dexter and Schulman.

The case of forbidden transitions. In the above case we assumed dipole–dipole interactions, i.e. transitions in S and A were both allowed. This gives the dependence of P_{SA} on distance as $1/R^6$ as in Van der Waals interaction of this kind.

$$P_{SA}(dd) \propto \frac{1}{R^6}$$

If the transition in the activator ion is of electric quadrupole type, the dependence on distance will be determined by a dipole–quadrupole Van der Waals interaction and

$$P_{SA}(dq) \propto \frac{1}{R^8}$$

and if both transitions are of quadrupole type we have

$$P_{SA}(qq) \propto \frac{1}{R^{10}}$$

Dexter and Schulman have shown that such transfers will occur with a significant probability. If a is a quantity of the order of the activator dimensions, then

$$\frac{P_{SA}(dq)}{P_{SA}(dd)} \approx \left(\frac{a}{R}\right)^2$$

which is about 1/10 for near-neighbour positions

$$\frac{P_{SA}(qq)}{P_{SA}(dd)} \approx \left(\frac{a}{R}\right)^4$$

In the latter case the life time τ_S is itself increased in the ratio:

$$\frac{\tau_S(q)}{\tau_S(d)} \approx \left(\frac{\lambda}{a}\right)^2$$

so that the (qq) transfer distances are essentially of the same order as those for (dd) transfers, while ten times higher activator concentrations are effective in (dq) transfers.

In contrast to all this, when the activator transition is of magnetic dipole nature Dexter finds that resonance transfers only occur for such high concentrations that transfer will occur by electron exchange processes.

II. OTHER TYPES OF ENERGY TRANSFER WITHOUT CHARGE DISPLACEMENT

1. Reabsorption of emitted light

If the activator centre A emits radiation which can be absorbed and excite another emission centre B, then a *secondary fluorescence* will occur from B. In gases the effect is inevitable and is most important. We can recall the recent experiments of A. Kastler, J. Brossel and J. P. Barrat on the apparent life time of the 6^3P_1 state of mercury atoms excited by 2,537-Å resonance radiation: this life time measured by paramagnetic resonance techniques (duration of coherence) is considerably increased by multiple diffusion when the mercury pressure is increased.

In inorganic phosphors the reabsorption effect is always possible and often difficult to eliminate. The most important practical case is that when the activators A and B are identical. The interaction between the luminescence centre and neighbouring ions is often so large as to give a considerable Stokes shift, and then the overlap of absorption and emission spectra is negligible. In sensitization effects even a small overlap of the ε_S and α_A spectra is sufficient to effect resonance transfer, but if one of the activator transitions is forbidden, which is often the case, then the reabsorption effects may become very small.

The case of zinc sulphide phosphors. As a general rule, a perfect zinc sulphide crystal sample is almost transparent to its own *visible*

emission. However, for most powdered ZnS phosphors, the radiations from 4,000 to 5,400 Å are slightly absorbed: this results in the excitation of a short duration phosphorescence (Lenard's 'Momentananregung'). Ritschl has succeeded in observing it under excitation by green light (5,350 Tl-line and 5,461 Hg-line), but with a small intensity and only when a special experiment is arranged to observe it.

On the other hand, the reabsorption of the *infra-red* emission of ZnS is not negligible; similarly the red emission of ZnS(Cu, Ga) is reabsorbed and leads to the excitation of the infra-red emission bands (Halsted, Apple and Prener).

2. Transfer by electronic exchange between neighbouring atoms

Since 1889 (B. Walter) it has been assumed that to explain *concentration quenching* of luminescent molecules pairs or aggregates of molecules are formed which are supposedly non-luminescent. Johnson and Williams have made a systematic study of this quenching mechanism in inorganic phosphors. They assume that an activator centre is not luminescent if there is another at the nearest z points of the surrounding lattice.

The approach of an activator B to within a distance r of an activator A can perturb the respective probabilities of radiative emission p_r and non-radiative energy dissipation p_{nr} of A.

Since the overlap integral

$$\int \psi_A \psi_B \, d\tau$$

varies exponentially with r, Johnson and Williams[†] postulate that

$$p_{nr} = s \exp\left(-\frac{E(r)}{kT}\right)$$

$$E(r) = E(\infty)(1 - e^{-\alpha r})$$

They then give the variation of the efficiency

$$\eta = p_r/(p_r + p_{nr})$$

as a function of activator concentration for the following:

$$
\begin{aligned}
&\text{in } ZnF_2(Mn) \quad \text{with } z = \quad\;\; 22 \\
&\text{in } KCl(Tl) \quad\;\;\; \text{with } z = \quad 150 \\
&\text{in } ZnS(Cu) \quad\;\; \text{with } z = 4{,}000
\end{aligned}
$$

In the latter case the high value of z reflects the low activator

† The physical ideas of this model are the same as in the 'shell model' for explaining the concentration quenching of fluorescence in solutions, but the mathematical formulation is different (see especially Jablonski, 1957).

concentration, about 2×10^{-4} Cu per ZnS for optimum efficiency. This leads to a distance between neighbouring centres of about 100 Å. It seems difficult to accept this size of the extension of individual centres, but by assuming the model of Johnson and Williams, that pairs of centres form the quenching centres, we can assume that for extinction it is not necessary for all the luminescence centres to form pairs. It is sufficient that the excitation energy of an isolated activator can be transferred to one of these pairs (either by resonance or hole migration).

In the case of gases and of organic solutions, collisions between luminescent and quenching molecules will enter into transfer processes. Such collisions can be eliminated from considerations of luminescent crystals.

III. TRANSFER OF ENERGY BY POSITIVE HOLE MIGRATION

The movement of positive holes in photoconducting phosphors gives an explanation of energy transfers over relatively large distances.

1. Riehl's excitation mechanism

Positive hole motion was first used (Riehl) to explain the excitation of luminescence activator centres by radiation absorbed in the fundamental absorption band of the crystal lattice (in ZnS-wurtzite $\lambda \leqslant 3{,}350$ Å; in CdS $\lambda \leqslant 5{,}100$ Å) and not in an absorption band due to the centres.

The excitation creates positive holes in the valence band and these then diffuse into the neighbourhood of the centres. If the electron in the centre falls into the hole, then this gives a state of excitation with the centres empty and conduction electrons available for recombination with the centres and production of luminescence emission.

If traps exist close to the centres, then in the Riehl mechanism they will not be preferentially filled by excited electrons (see the paragraph on phosphorescence kinetics).

Fig. VIII.2 *Excitation of a centre after absorption of radiation lying within the fundamental absorption band of a crystal lattice (Riehl)*

The quantum efficiency of the luminescence is about 20–30 per cent under excitation by Riehl's process. It is a constant when the wavelength of the exciting radiation is changed and remains in the fundamental absorption region of the crystal (Antonov-Romanovsky and Alentsev). On the other hand, when the exciting radiation falls in the proper absorption band of the Cu centre, the efficiency is higher and often approaches unity.

2. The Schön-Klasens theory of energy transfer between two centres

Consider the 'de-activation' of a luminescence centre (e.g. Cu in ZnS) by a 'killer' centre (such as Ni). We have, then:

(*a*) Thermal activation of an electron from the valence band into an empty copper centre which needs an energy W which determines the probability of the transfer.†

(*b*) Movement of the positive hole created in the valence band.

(*c*) An electron from the nickel centre falls into, i.e. annihilates, the positive hole and leaves the nickel centre empty.

We do not normally assume resonance transfer to occur in these phosphors because the transfer distances are too great. The quenching or 'killer' action of nickel is easily observed at concentrations of 10^{-6} g Ni per g. ZnS which corresponds to an average distance between 'killer' centres of 400 Å. For resonance this would have to be of the order of 35 Å.
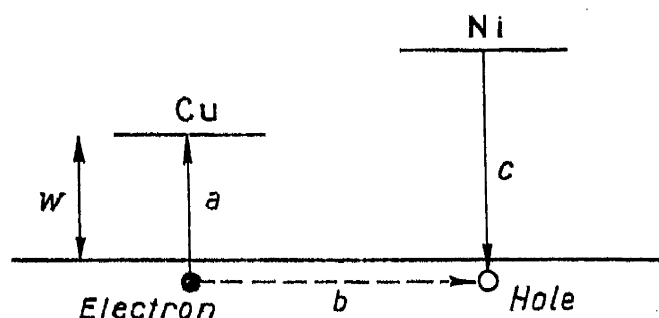
Fig. VIII.3 *Energy transfer by hole migration according to the Riehl–Schön-Klasens mechanism*

The discovery of the photomagnetic effect in CdS has provided

† In recent studies on the analogous problem of the transfer between blue (Zn-vacancies) and green (copper) centres in ZnS(Cu, Cl) phosphors, Melamed (1958) has given evidence for the possibility of such a transfer to occur even at very low temperatures (4°K). This fact leads to the assumption that the excitation itself produces holes in the valence band and the thermal activation W is not necessary; radiation of $\lambda = 3,450$ Å was used for this excitation and was thus not able to excite electrons directly from the valence band to the conduction band according to Riehl's mechanism, but probably able to raise electrons to empty localized levels in the forbidden band.

However, if the temperature is high enough and thermal activation occurs, the efficiency of the transfer process is enhanced.

direct evidence of hole motion. However, in CdS the Kikoin poten-
tials are of the order of a few microvolts, while in germanium they
exceed 10 millivolts. The hole mobility is thus very small. Experi-
mental studies have given a value of the ambipolar diffusion coeffi-
cient:

$$D \approx \frac{\mu kT}{e}$$

$$\frac{2}{\mu} = \frac{1}{\mu_{\text{holes}}} + \frac{1}{\mu_{\text{electrons}}}$$

It is found that

$$\mu \approx 2 . 10^{-4} \text{ cm/sec per volt/cm in CdS}$$

while in germanium

$$\mu \approx 2,300 \text{ cm/sec per volt/cm}$$

If we assume a carrier life time of 10^{-5} sec in CdS, we can obtain
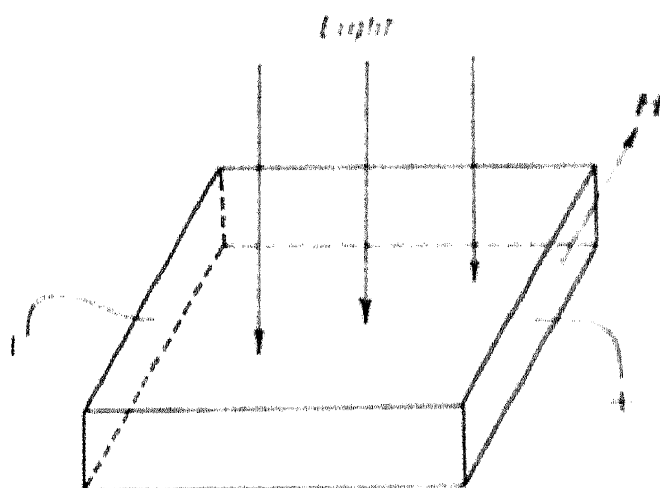
Fig. VIII.4 *Photoelectromagnetic effect (Kikoin effect)*
The specimen is irradiated on its surface, holes and elec-
trons diffuse into the crystal: if the diffusion current is
deflected by application of a magnetic field parallel to the
illuminated surface then a potential difference appears
across the width of the specimen

D from μ, and finally the diffusion length L from the Einstein relation:

$$L = \sqrt{D\tau}$$

We find that

$$L \approx 750 \text{ Å in CdS}$$

which is much smaller than that in germanium

$$L \approx 1/50 \text{ cm}$$

but is still sufficient to justify the effects of hole migration.

In the main we can say that

(*a*) in photoconducting phosphors charge migration will predomi-
nate in energy transfer;

(*b*) in phosphors with transitions within well-defined centres (such
as rare earth impurities) resonance transfer will predominate.

This is only a rough approximation and the different modes of trans-
fer can occur at the same time.

IV. ENERGY TRANSFER BY EXCITON MIGRATION

We now return to the transfer process between a sensitizer S and an
activator A. Another process in which an electron on S returns to its
ground state, while that on A is raised to an excited state, can be
described in two stages:

(*a*) the return of the electron on S creates an exciton which diffuses
to A;

(*b*) the exciton is absorbed at A and raises an electron into the
excited state.

We can assume the emission of an actual exciton which can be
detected by its diffusion or a *virtual* exciton, i.e. there is no conserva-
tion of energy in two processes a and b (simply energy conservation
over the whole transfer process). These two cases have been con-
sidered by H. Haken.

Transfers by real excitons are naturally more interesting; the intro
duction of virtual excitons is no more than a mathematical device to
describe the matrix elements occurring in the evaluation of the
transfer probability.

A notable experiment by Broser and Balkanski shows the possi-
bility of the action of excitons at large distances from their point of
creation. They irradiated one part of a platelet of CdS through a
narrow window in an opaque screen. The radiation was of too low
a quantum energy to bridge the energy 'gap' of the crystal and there-
fore to produce photoconductivity. However, it can produce excitons
which diffuse and finally dissociate at impurity levels and liberate
electrons and holes. Thus photoconduction is observed in the region
of the crystal where the excitons dissociate.

At a distance x from the irradiated area the exciton density in the
steady state is

$$\rho = \rho_0 \, e^{-x/L}$$

The observed photocurrent varies with separation of the electrodes

from the illuminated area according to a relation of the above form. The measurements give directly a value for the exciton diffusion length:

$$L = 0 \cdot 23 \text{ cm in CdS}$$

Experiments show that the excitation spectrum for the photoconduction has hydrogenlike features and is identical with the absorption spectra attributed to exciton formation. In addition, application of
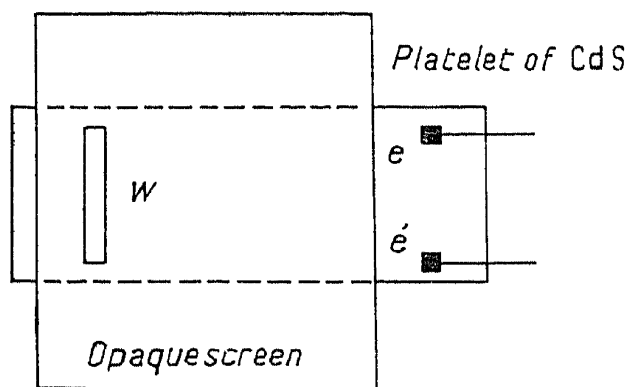
Fig. VIII.5 *Experimental arrangement used by I. Broser and M. Balkanski*

The platelet of CdS is irradiated through the window W and a photocurrent is observed between the electrodes e and e'

an electric field does not modify the diffusion process showing that neutral entities are involved. It is difficult to prove that the diffusing agent is not a photon, i.e. that photoconductivity is not excited by a secondary fluorescence. However, a distinction can be made if non-steady state experiments are made, the form of the signal being different for each case (M. Balkanski and A. Fortini).

Using a quantum energy greater than the crystal band gap, an intense photoconduction is observed due to free electron and hole creation.

Exciton migration over large distances is only possible in very pure and defect-free crystals. It is particularly sensitive to the presence of surface states.

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Electroluminescence and

Electrophotoluminescence

The production of luminescence solely by the action of an applied electric field on a material is known as *electroluminescence*. The various effects known to date for crystalline solids can be divided into two main categories as follows:

1. 'Pure' or 'intrinsic' electroluminescence (the Destriau effect), which is the result of the sole action of the applied electric field, as in electroluminescent cells or panels. These are made by dispersing a suitable phosphor powder in a suitable dielectric in a condenser system, an alternating field being applied to the electrodes.

2. Electroluminescence due to charge carrier injection. This is the emission produced by injection of charge carriers through a rectifying contact such as a 'cat's whisker' contact on a crystal or a P–N junction. A current passes, the luminescence intensity being approximately proportional to this current. In contrast, for intrinsic electroluminescence the phosphor need not be in contact with the electrodes and no net current passes through the crystals.

The term electrophotoluminescence was originally reserved for the Gudden and Pohl effect, i.e. for the transient luminescence occurring when an electric field is applied to a phosphor previously excited by, say, ultra-violet or X-radiation. A number of effects produced by the action of electric fields on photoluminescence may be grouped under this term, some of them permanent, the field causing quenching or stimulation of emission during photo-excitation.

I. 'PURE' OR 'INTRINSIC' ELECTROLUMINESCENCE

1. Introduction: description of phenomena

Historical. The circumstances of the discovery of electroluminescence are worthy of mention here. In 1936 G. Destriau completed his

Doctorate Thesis at the Radium Institute in Paris. It was concerned with scintillations produced by α particles in zinc sulphides. The experiments showed that the fluctuations in α-particle range were larger when measured by the scintillation method than by any other method, e.g. using ionization chambers. Destriau explained this difference by the fact that the fluctuations in the number of excited centres due to each α particle and in the scintillation yield correlated with the fluctuations in particle range. In the course of this work he wished to compare the ionization of the crystal lattice by an intense electric field with that produced by the α particles: it was in this way that he saw the illumination of the sulphide under the action of the field and in the absence of α-particle excitation.
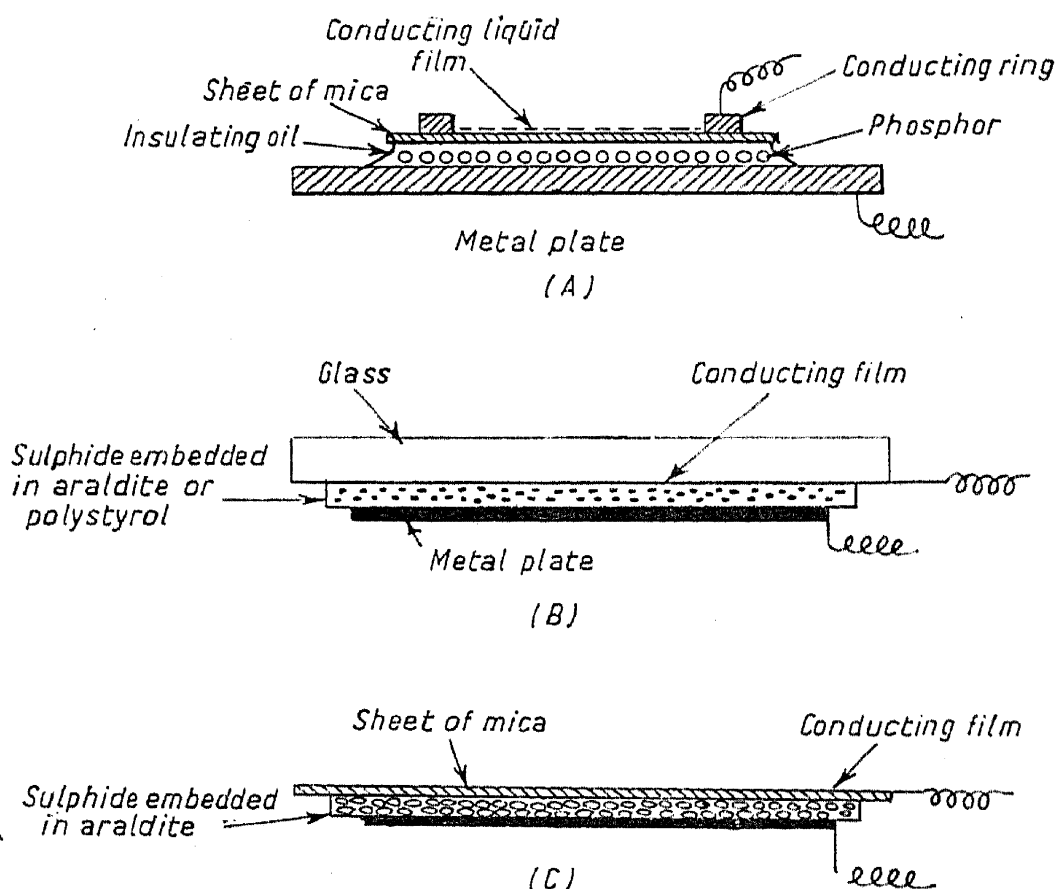
Fig. IX.1 *Various kinds of electroluminescent cells*
A *Cell originally used by G. Destriau*
B *Electroluminescent lamps using conducting glass*
C *Cells used by J. Mattler for study of effect of temperature on electroluminescence. A high concentration of zinc sulphide to dielectric binder is arranged. To avoid charge injection effects the transparent electrode is a thin sheet of mica and the mixture ZnS + araldite is deposited on the non-conducting face*

Production of electroluminescent 'cells'. The first cells constructed by Destriau were very delicate. The phosphorescent sulphide was included in a liquid dielectric (castor oil) and the transparent electrode necessary to see the emission was a sheet of mica covered with salt water.

The development of conducting glass or mica† enables more robust cells to be made which are used in commercial applications (electroluminescent lamps). The zinc sulphide is embedded in a plastic dielectric (e.g. araldite or polystyrene) or in a ceramic. A condenser is made by putting such a dielectric layer between two electrodes, one of conducting glass or mica and the other a deposited metal layer or by metal foil.

The thickness of the dielectric layer is about 0·1 mm. Usually about 200 V is applied to the cell giving an average field of 20,000 V/cm. However, the field inside the sulphide crystal grains will depend on the dielectric. If a voltage V is applied to the cell of thickness d, then $E_m = V/d$, the mean field. For spherical grains of ZnS of dielectric constant K_1 in a dielectric of dielectric constant K_2, the field E_{ZnS} in the grains is given by

$$E_{ZnS} = E_m \cdot \frac{3K_2}{2K_2 + K_1 - v(K_1 - K_2)}$$

where v is the fraction of the total volume occupied by the sulphide grains. Actually the crystals are angular in form and their internal field is very far from homogeneous, even leaving aside the problem of potential barriers in or on the crystal grains.

Emission spectra. In general, we find the same luminescence emission bands as in photoluminescence, for example, the blue and green bands of zinc sulphide.

The positions of the respective maxima of the different bands show only minor changes with the kind of excitation. For example, when the applied field is increased, definite displacements occur towards the red which are due to the Stark effect on the luminescence centres.

However, the relative intensities of the different emission bands can show considerable variations (Fig. IX.2).

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† To make conducting glass (U.S. Pat. No. 2-522, 531 19th Sept. 1950) a glass plate is heated to about 600° and then on its surface is sprayed a hydrochloric acid solution of stannic chloride containing a little antimony trichloride. There then forms on the surface a thin, very adhesive and transparent layer of tin oxide of small resistance (about a few ohms over the cell surface).

Often, as shown in this figure, the blue emission band of a ZnS(Cu) phosphor can be enhanced relative to the green band in the electroluminescence spectrum, or in cathodoluminescence compared with the photoluminescence spectrum. For instance, Destriau and Ivey
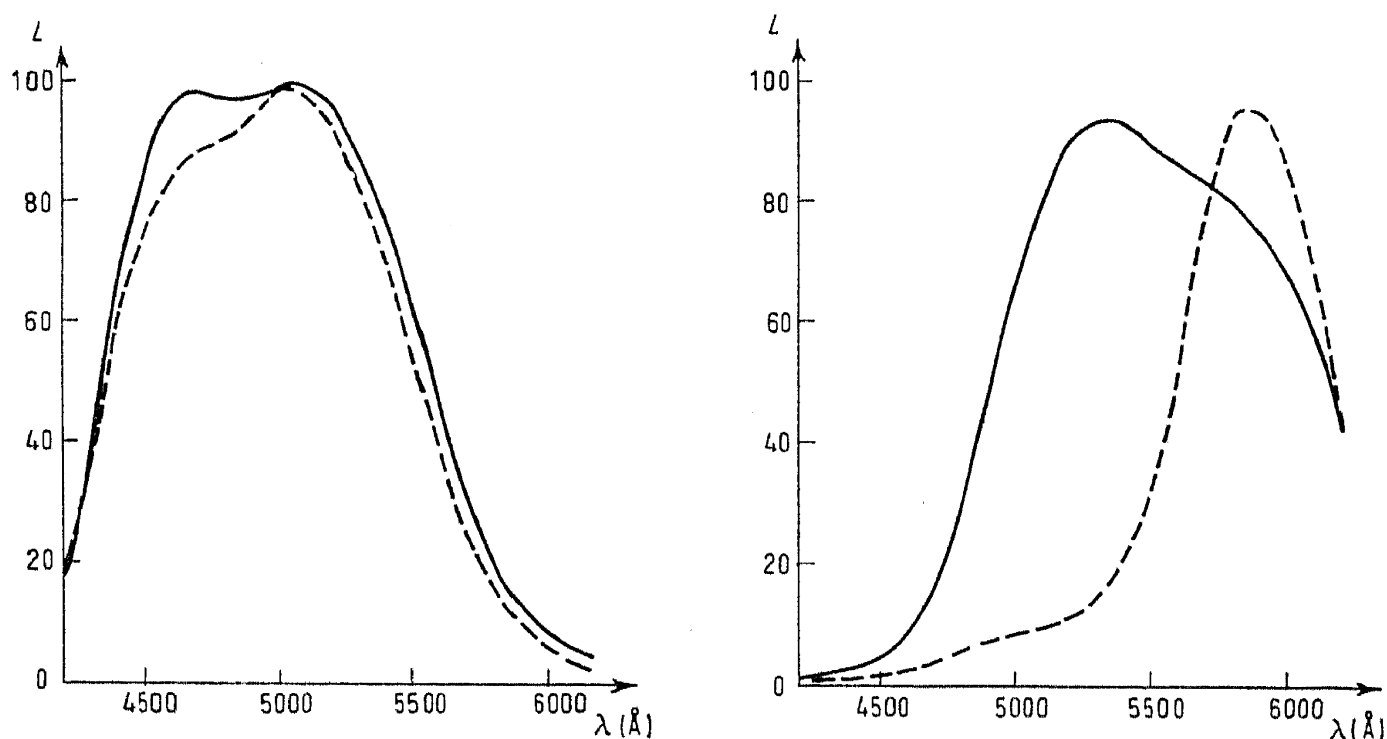
Fig. IX.2 *Emission spectra of a sulphide phosphor in photoluminescence (dotted curve) and in electroluminescence (full line)*

A *ZnS(Cu) with 'blue' and 'green' centres. Applied field frequency 20 c/s*

B *ZnS(Cu, Mn) with green (Cu) and orange-yellow (Mn) bands. Applied field frequency 50 c/s*

(*After J. Mattler and T. Ceva*)

have described a sulphide in which the two bands had similar intensities under 3,650-Å radiation; however, the blue band became predominant in electroluminescence.

When the temperature is increased, the blue band is quenched before the green band, whatever the type of excitation.

When the frequency of the applied field is increased the intensity of both bands increases; but the green band soon shows a saturation effect while the blue band continues to increase. Thus generally a ZnS(Cu) electroluminescent phosphor which shows a dominant green band at a frequency of 50 or 60 cycles/sec shows a blue emis-

sion at the frequency of about 2,000 cycles/sec. We shall return later to these saturation phenomena.

Variation of brightness with applied voltage. The variation is very marked (exponential). Destriau proposed in 1937 an empirical formula of the following form:

$$L = L_0 \exp\left(\frac{aV+b}{cV+d}\right) \tag{1}$$

then, on the suggestion of Jean Perrin, he used only the more simple form:

$$L = L_0 \exp\left(-\frac{B}{V}\right) \tag{2}$$

The agreement of the expression in equation (2) with experiment is sufficiently good over several decades of light intensity L. The importance of this expression is that it can be given a very simple interpretation and leads to that actually assumed for the phenomenon of electroluminescence: *that is, excitation of the luminescence centres by the collisions of accelerated electrons.*
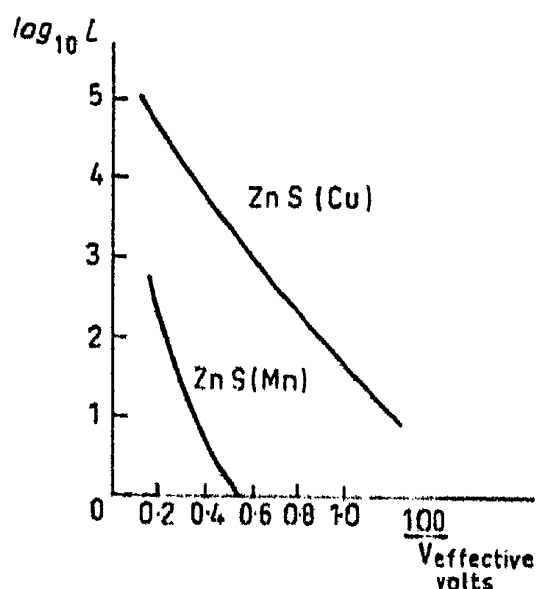
Fig. IX.3 *Variation of luminance L of electroluminescent phosphors ZnS(Cu) and ZnS(Mn) with applied voltage V (After G. Destriau)*

When an electron with charge e traverses a path x in the direction of the field E, it acquires a kinetic energy:

$$E_{kin} = eEx$$

If W is the energy for an accelerated electron to excite or ionize a

luminescence centre in collision, the path x must be great enough for

$$E_{kin} > W$$

that is

$$x > l \quad \text{with} \quad W = eEl$$

If $\bar{x}$ denotes that mean free path for the accelerated electrons, the fraction of electrons with paths greater than l is

$$f = \exp\left(-\frac{l}{\bar{x}}\right)$$

The brightness L is proportional to this fraction f, that is

$$L \propto \exp\left(-\frac{b}{E}\right)$$

with

$$b = \frac{W}{e\bar{x}}$$

Of course, the field E inside the crystal will not be exactly proportional to the applied field. In addition, other factors than the fraction f will affect the brightness. This is why the formula (2) cannot be exact. Nevertheless, it must be conceded that it is the proportion f of the accelerated electrons which determines the luminescence emission.

Besides the factor $f = \exp(-b/E)$, we must introduce into the expression for L

the number $n(E)$ of accelerated electrons;

the probability p that the collision of a sufficiently energetic electron with a centre will result in the excitation of the latter;

the efficiency η of the resultant radiative recombinations.

We can therefore write

$$L(E) = n(E) . f(E) . p\eta$$

Because of the inhomogeneity of the field inside the crystal, and the variation of this during a voltage cycle, we cannot apply such a simple formula to describe accurately the relation between L and V.

In spite of this, the semi-empirical expressions of simple form have some interest.

As a modification of equation (2), Destriau proposed the following:

$$L = L_0 V^n \exp\left(-\frac{b}{V}\right) \tag{3}$$

Following Zalm, Diemer and Klasens (1954), many authors have

used the following formula:

$$L = L_0 \exp\left(-\frac{b}{\sqrt{V}}\right) \quad (4)$$

or again that of Alfrey and Taylor:

$$L = L_0 V^n \exp\left(-\frac{b}{\sqrt{V}}\right) \quad (5)$$

This formula is interpreted by assuming that the luminescence emission results mainly from the existence of a potential barrier of the Mott–Schottky type, where the field E is proportional to $\sqrt{V}$.

The agreement of the formula (4) with experiment is often very good (Fig. IX.4).

Nevertheless, Lehmann (1960) has shown that if the crystal grains of zinc sulphide are separated according to their diameter, the luminescence due to grains of the same dimension is less than the luminescence for the whole powder in the relation of (4). He has also shown that the luminescence of a single particle of phosphor follows the relation involving $\exp(-b/V)$ and not that involving $\exp(-b/\sqrt{V})$. For an isolated particle one need not assume

Fig. IX.4 *Variation of luminance L of a ZnS(Cu) phosphor with applied voltage V (After Zalm, Diemer and Klasens)*

the existence of a Mott–Schottky barrier, but such particles give less emission than those in contact with the electrodes (D. Curie, 1953).

It must also be true that for small voltages the field is not sufficient to produce electroluminescence except in the surface barrier (the Mott–Schottky barrier or an intrinsic barrier). However, at high voltages the luminescence emission can occur from the whole of the crystal. According to a suggestion from Thornton, for an electroluminescent cell of the usual type, the relation including $\exp(-b/\sqrt{V})$ is valid at small voltages and the relation including $\exp(-b/V)$ is applicable to high voltages. This is very obvious in the results of the experiments of Antonov-Romanovsky (1959).

As expected from all the above empirical formulae, there is no threshold for the electroluminescence effect: when the emission is no longer visible to the naked eye it can still be detected by means of a photomultiplier and it can be shown that the change with voltage goes on without a discontinuity (Destriau and Domergue). The apparent observed threshold depends on the sensitivity of the detector.
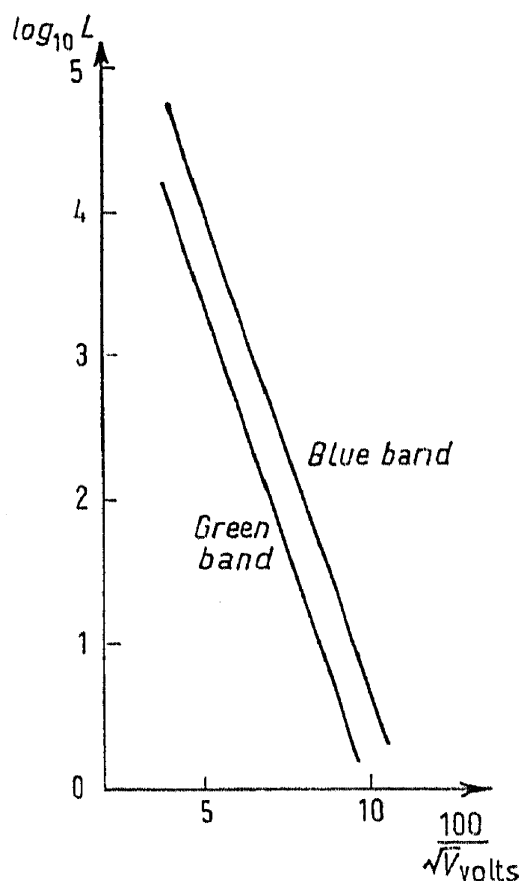
Fig. IX.5 *Parallel variation of the green and blue emission bands of a ZnS(Cu) phosphor with applied voltage*
(*J. Mattler and T. Ceva*)

To obtain this data rigorously the displacement of the bands as the voltage is varied must be allowed for. Interposition of blue or green fillers in front of the measuring photomultiplier does not give the exact parallelism

The case of sulphides with several activators. Different emission bands behave in a different way with applied voltage. For instance, in ZnS(Cu, Mn) the band associated with copper predominates at low voltages and that due to the manganese at high voltages.

In contrast, the green and blue bands of ZnS(Cu) change in a similar way, showing that the same energy W is required to excite the two different kinds of centres due to copper (Fig. IX.5).

Brightness waves. We obtain an insight into the mechanism of electro-luminescence by presenting simultaneously on a double-beam oscillo-graph screen the emission brightness wave and the voltage wave.

If in the dielectric around the crystal there exists a sinusoidal field E_0 of frequency $f = \omega/2\pi$, Destriau has shown in his early investiga-tions that the field E in the zinc sulphide leads E_0 in phase with an angle ϕ given by

$$\tan \phi = \frac{4\pi}{K\rho\omega} = \frac{2}{K\rho f}$$

where K is the dielectric constant and ρ the resistivity of the sulphide. The magnitudes of both fields are given by

$$E = E_0 \cos \phi$$

Later on, Destriau and Ivey showed that the field E_0 is itself lag-ging behind the applied voltage V, by an amount which is complex in interpretation and subject to assumptions about the shape of the crystals, &c. However, if the relative amount of sulphide embedded in the mass of dielectric is small, E_0 is in phase with V and the differ-ence in phase between the internal field and V is simply equal to ϕ.

Experiment shows clearly a shift in a leading direction of the brightness maximum with respect to the voltage maximum.
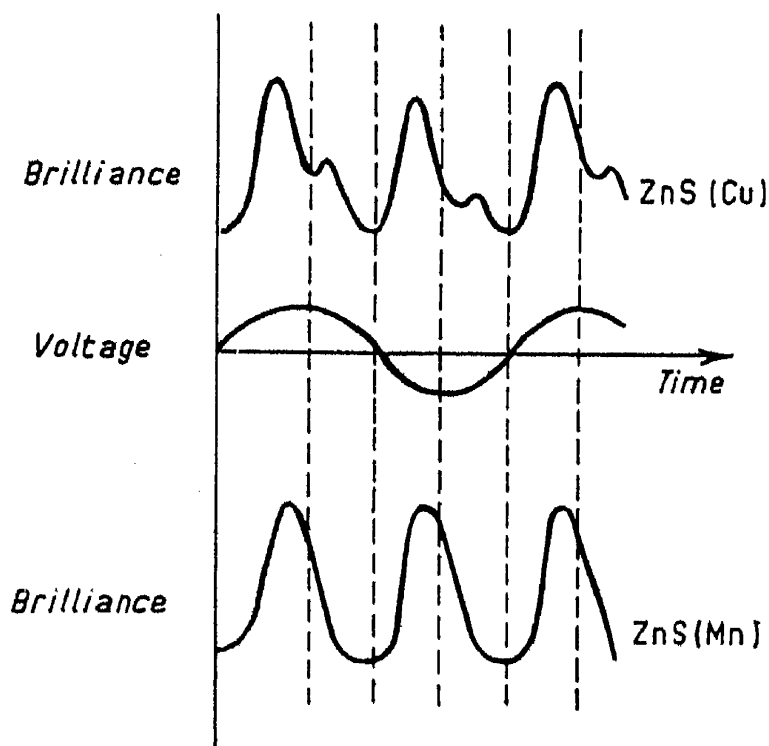
Fig. IX.6 *Brightness waves obtained for ZnS(Cu) and ZnS(Mn) in an alternating applied field (G. Destriau)*

I

The resistivity ρ varies during the voltage cycle, and in contrast to the maximum, the minimum of the brightness is often found in phase with the zero of the voltage V.

The simple form of the brightness waves obtained for ZnS(Mn), where there is direct excitation of the luminescence centres, without ionization, contrasts with the occurrence of a secondary brightness maximum observed almost always for the ZnS(Cu) phosphors where the centres are ionized. The secondary maximum is related to electrons which recombine with the centres after a delay, for example, because they have been trapped; the intercrystalline contacts also have an effect on the brightness of this maximum.

If a steady voltage is applied to the cell the internal field becomes zero, and a weak continuous emission results. This is characteristic of pure electroluminescence.

Phosphors used in electroluminescence. Zinc sulphides showing a good electroluminescence are relatively rare. At the voltages used, which are often much smaller than those causing dielectric breakdown, the acceleration of electrons from thermal energies up to those of several electron volts necessary for excitation of the centres is a relatively rare event.

Recipes have been given for the preparation of good phosphors. We shall discuss these after looking a little more at the mechanism of the phenomena.

Most often zinc sulphide activated by copper, silver or manganese is used. The respective emission bands are in the green and the blue regions for copper and in the blue for silver and the yellow-orange region for manganese.

Addition of cadmium sulphide to zinc sulphide causes the emission bands to be displaced towards longer wavelengths (see page 120); however, generally the electroluminescence of solid solutions of ZnS and CdS is not as good as that for ZnS (Zalm). The electroluminescence of cadmium sulphide has been observed, but under conditions which more nearly approach dielectric breakdown than in ZnS (K. W. Böer and Kummel, G. Diemer); in other experiments, electroluminescence arises by the injection of charges followed by electron hole recombination (R. W. Smith).

It is likely that cadmium sulphide is too good a conductor for the internal field to be high, except in the neighbourhood of breakdown voltages.

A. Wachtel (1960) has shown that for a ZnS+HgS phosphor, activated with copper, a red electroluminescence can be obtained which completes the gamut of colours which can be obtained in electroluminescence.

To have a greater flexibility in the realization of various colours, a simple process is available (H. F. Ivey); it is sufficient to embed the electroluminescent sulphide in a dielectric which has been coloured by an organic dye. The latter is not usually electroluminescent but acts as a colour filter for the light emitted by the sulphides.

In most sulphides, oxides and silicates of zinc (willemites activated by manganese) the Destriau effect is observed. Their emission is green. In this group we should include the selenides and tellurides of zinc and cadmium.

The efficiency and application of electroluminescent cells. Electroluminescence is the *direct conversion of electrical energy into visible light.* However, the efficiency is low, which is easily explained by the theory of centre excitation by collisions of accelerated electrons since this process has a low probability.

The efficiency reaches an optimum value for a given voltage† which depends on the size of the sulphide grains, on the construction of the cell and on the applied field frequency. Ivey and Lehmann have obtained values approaching 15 lumens per watt.

It is thought that this value may be doubled. Because of the low efficiency, applications are limited at present to dispositions with low brightness such as safe lamps, dashboards, &c.

Fig. IX.7 *Efficiency of a ZnS(Cu) cell as a fraction of applied voltage (Ivey and Lehmann)*

The lighting of a room by means of a ceiling or walls entirely made of electroluminescent cells provides in a direct way the advantage of indirect lighting: the absence of dazzles, shadows, &c. Moreover, if

† In contrast, when the brightness is proportional to the frequency (absence of saturation effects), the efficiency is independent of frequency (W. Lehmann).

cells with different activators are used, the colour of the luminescence can be changed at will by altering the voltage or the frequency of the supply.

2. Discussion of the electroluminescence mechanisms

The excitation process for the luminescence centres involves three parts (Piper and Williams, D. Curie):

(*a*) The raising of electrons for acceleration into the conduction band.

(*b*) Acceleration of some of these electrons by the field.

(*c*) Collision of these electrons with centres causing the excitation or ionization of the latter.

Finally, the radiative or non-radiative recombination of electrons with centres will occur.

We now consider in turn these different processes:

(*a*) *Raising of electrons into the conduction band.* These electrons come from donor levels which are deeper than the traps (which are empty in the unexcited sulphide) but not as deep as the centre levels. We can assume that their depth is about 1 or 1·2 eV.

The question is, are these levels emptied by thermal activation or by the action of the field?

If a purely thermal activation occurs, the electroluminescence would be dependent on the temperature and involve a high activation energy, but this is not the case (Fig. IX.8). It must be due to a direct emptying of the donor levels by the field which is, as obvious, incapable of exciting the centres directly.

Piper and Williams have shown that for such emptying of the donor levels an electric field of about 200,000 V/cm would be necessary; such a field could not occur throughout the interior of the crystal but would probably exist in the potential barrier (Mott–Schottky or intrinsic).

According to an idea of Frenkel, the field and the phonons mutually assist each other in producing ionization of the levels in the following way: if the depth of the level is ε in the absence of the field, the probability of ionization per second is

$$p = s \exp\left(-\frac{\varepsilon}{kT}\right)$$

which is very small if ε is large. In the presence of the field E the depth is reduced to

$$\varepsilon^* = \varepsilon - f(E)$$

and the probability of ionization becomes

$$p = s \exp\left(-\frac{\varepsilon - f(E)}{kT}\right)$$

During the first few cycles of the applied field on the cell the brightness is very low (F. Vigean and D. Curie). Gradually the electrons fall into the traps which at the beginning are empty, and the ionization of the latter by the same process as above soon plays a dominant role in
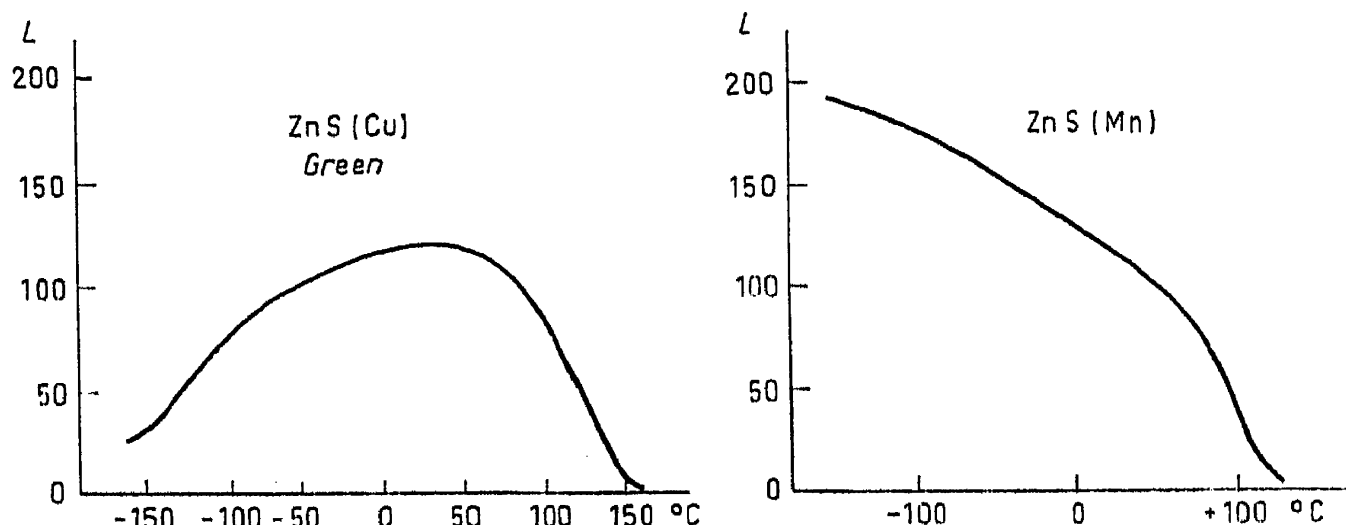
Fig. IX.8 *Variation of brightness of electroluminescent sulphides with temperature (J. Mattler)*

A rise in temperature decreases the mean path of electrons between thermal collisions and tends to prevent their acceleration: in contrast the liberation of donor level electrons into the conduction band by the field is made easier. The two effects act in opposite directions. In addition normal thermal quenching of emission occurs. Haake has shown how corrections may be made to obtain the effects really due to the electroluminescence processes

the supply of electrons to the conduction band. Thornton and Haake have shown that the thermal activation of the trap of depth $\varepsilon = 0.3$ eV which gives the electroluminescence L must be replaced by a thermal activation with an energy ε^* which varies with the voltage and the frequency of the applied field, ε^* being of the order of a few hundredths of an electron volt, sometimes greater, but always less than ε.

(b) *Acceleration of the electrons by the field.* The condition for an electron to accelerate is that it must gain energy more rapidly in the field than it loses by interaction with phonons; if ε is the energy of such an electron:

$$\left(\frac{d\varepsilon}{dt}\right)_{\text{field}} > \left(\frac{d\varepsilon}{dt}\right)_{\text{phonons}}$$

If w is the path between two phonon encounters, at the end of the path w, the electron exchanges with the phonon an energy $h\nu$. We can write the condition for acceleration in the form due to Frölich and Mott:

$$\mathrm{e}Ew > h\nu\left[1 + \frac{2}{\exp(h\nu/kT) - 1}\right]$$

Unfortunately w is not at all well known for zinc sulphide; it is probably of the order of 10^{-7} cm for the thermal electrons but this lack of information does not permit any precise discussion at the moment about the field intensity capable of producing the acceleration. Nevertheless, we can be sure that most of the thermal electrons are not accelerated by fields less than 100,000 V/cm. Some of them
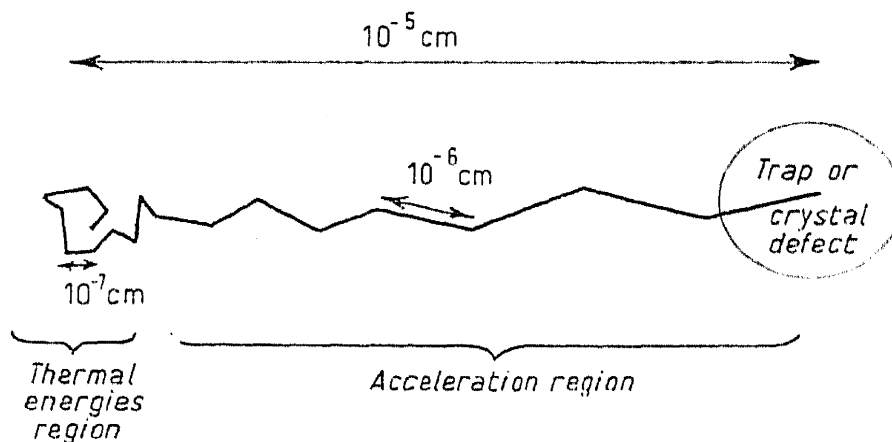
Fig. IX.9 *Path of an accelerated electron in the conduction band*

will always be able to reach an energy of the order of several tenths of an electron volt because of the fluctuations: for instance, at the end of a path greater than the mean length w or at the end of a suitable interaction in which energy is received from the phonons rather than lost to them.

The important point is as follows: in ionic crystals the mean free path rises gradually and is proportional to the energy of the electrons.† Thus an electron which begins to be accelerated and crosses the critical zone at about a tenth of an electron volt has a mean path greater than 10^{-6} cm, and the process of acceleration continues even in fields of the order of 20,000 V/cm.

On the other hand the interactions, which are sensibly isotropic at low energies, only occur with low-angle scattering at higher energies

† It rises even faster at high energies where $w \propto E^2$.

and the path finishes by being a straight line effectively in the direction of the field.

Thus, in an ionic crystal in an electric field of the order of tens of thousands of volts per centimetre, we can distinguish two electron groups:

(*a*) the greater part of the electrons remaining at thermal energies, with an electronic temperature greater by a few degrees than the lattice temperature (this temperature does not show any effective increase except when the conditions for dielectric breakdown are approached);

(*b*) some electrons, effective initially by favourable fluctuations in interactions, have a considerable temperature.

The introduction of the idea of the electronic temperature into electroluminescence is due to Nagy and Goffaux. We should notice that the expression given previously for the fraction of electrons with mean paths to greater than *l*:

$$f = \exp\left(-\frac{l}{\bar{x}}\right)$$

is the same as postulating a Boltzmann distribution for the group of hot electrons:

$$f = \exp\left(-\frac{W}{kT_e}\right)$$

$$kT_e = eE\bar{x}$$

where T_e is of the order of 4,700°K for $\bar{x} = 10^{-5}$ cm and $E = 40,000$ V/cm.

$\bar{x}$ and T_e are not limited by the thermal interaction which in this energy region no longer prevents the electron from being accelerated indefinitely. In particular, the loss of energy at a donor level or at a full trap when ionization of either occurs is a generator of *avalanches* for which the multiplication factor is naturally much less than that for avalanches leading to breakdown.

The stopping of the electron by a luminescence centre with excitation of the latter is a relatively rare phenomenon: in the example above, to have an energy W of 2·4 eV (the value for a quantum of green light), the electron must be accelerated over a path six times greater than the mean path $\bar{x}$, where $f = e^{-6} = 1/400$.

Only very rarely will an accelerated electron obtain sufficient energy to excite an electron from the valence band and to form a free electron hole pair. This is why no dielectric breakdown occurs.

(*c*) *Excitation of the centres by impact of a fast electron.* Impact of a fast electron with a luminescence centre involves the loss of the whole or part of its energy and the release of an electron from the centre into the conduction band (see Fig. IX.10).

Both electrons will have after impact some residual motion in the field direction. They will be in the same state as an electron beginning its acceleration and will be moved far from the original centre by the action of the field. This is borne out by Zalm's experiments. He applied a unidirectional field to an electroluminescent copper-activated zinc sulphide (the field oscillating between zero and a maximum
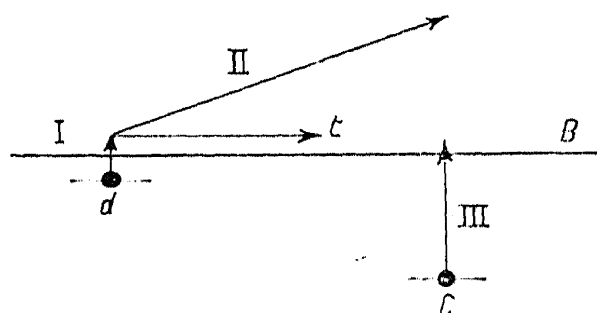
Fig. IX.10 *Schematic picture of excitation mechanism for electroluminescence due to accelerated electron impacts*

B *Conduction band*
d *Shallow donor level*
c *Luminescence centre*
  ι *Ionization of donor by electric field*
  ιι *Acceleration of some electrons raised into conduction band* (*t-path of electron remaining at thermal velocity*)
  ιιι *Ejection of electron initially in centre due to impact of an accelerated electron*

value). The maximum of the brightness wave does not occur at the field maximum but at the time when the field is zero and when the electrons return to their original centres (Fig. IX.11). However, in the case of ZnS(Mn) phosphors when the centres are mostly excited but not ionized the emission maximum occurs only a short time after the field maximum is reached, the displacement being clearly due to the life time of the excited state of the centre. Electroluminescence produced by fast electrons in the bulk of the phosphor is rather like cathodoluminescence, i.e. the traps are only slightly populated and the emission bands modify in the same way when compared to photoluminescence, &c. (this remark is due to Klasens). However, there are certain differences, notably the much lower value of the excitation

energy, the much higher ionization density and the removal of elect-
rons from the neighbourhood of the empty centres by the electric field.
*Recombination of freed electrons with empty centres: effect of applied
field frequency on electroluminescence.* For each cycle of the applied
field the donor ionization, electron acceleration and ionization of centres begins afresh. Within fairly wide limits the light sum in each cycle is constant and the brightness is proportional to the applied field frequency (J. Mattler, 1946). However, at high frequencies saturation effects occur which are more marked for the green band than for the blue band in ZnS(Cu) phosphors. If the

Fig. IX.11 *Brightness waves due to a unidirectional applied field* (P. *Zalm*)

frequency is too high the electrons liberated in any half-cycle have
not recombined before the following half-cycle occurs.

The brief calculation below, though rather over-simplified,[†] leads
to a formula which shows good agreement with experiment. Since the
freed electrons are removed some distance from the centres in the
excitation process we can assume a hyperbolic recombination pro-
cess. If $n(t)$ is the number of excited electrons remaining after time t.
then

$$n(t) = \frac{n_0}{(1+n_0\alpha t)}$$

where α is a constant, and n_0 the number of electrons initially excited.
In a time $t = 1/2f$ (f is the applied field frequency) the light sum S
is proportional to

$$n_0 - n(1/2f)$$

and the brightness is given by

$$B = S.2f$$

so that

$$B \propto \frac{n_0^2\alpha}{(1+n_0\alpha/2f)}$$

or

$$\frac{1}{B} \propto \frac{1}{n_0^2\alpha}\left[1+\frac{n_0\alpha}{2f}\right]$$

[†] In actual fact, all the electrons are not excited into the conduction band at
the same instant.

Thus $1/B$ is a linear function of $1/f$. If α is large, i.e. if the life time of conduction electrons is short compared with the period of the ap-plied field, then the straight-line graph of the relation will pass through the origin and B will be proportional to f. At low frequen-cies (below 50 c/s), systematic devia-tions occur from this relation due to polarization effects. The internal field is much smaller than the applied field and depends on the frequency. These effects can be de-scribed in terms of relations given previously:
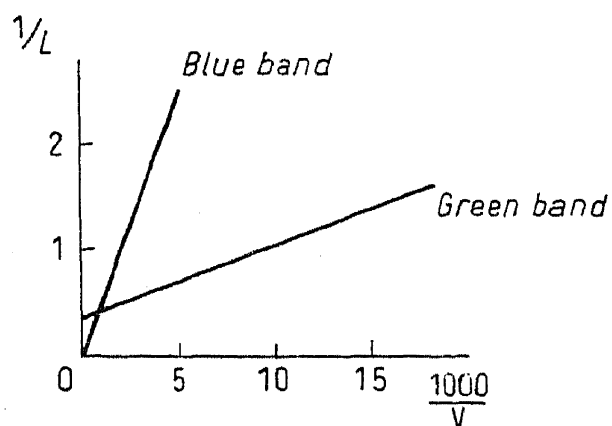
$$E = E_0 \cos \phi; \qquad \tan \phi = 2/K\rho f$$

Fig. IX.12 *Variation of in-tensities of blue and green bands of an electroluminescent ZnS(Cu) phosphor with applied field fre-quency*

The various regions present in an electroluminescent material: micro-scope and electron microscope studies. The above theory suggests that there should be three regions of interest in an electroluminescent layer:

(i) A region of high field strength (superficial or intergranular potential barriers) greater than 10^5 V/cm where direct ioniza-tion of traps or donor levels occurs due to the high field. This effect increases the number of conduction electrons.

(ii) A region in which these electrons are accelerated and excite the luminescence centres where the field is greater than 10^4 V/cm. In this region the luminescence emission occurs. At low volt-ages it occurs in the potential barrier, but at high voltages it extends right across the crystal grains.

(iii) A dark region where the field is low, less than 10^4 V/cm. Electrons removed from centres and donor levels move into this region, their energies remaining at thermal equilibrium values. They can only return to the second region when the field reverses. They become trapped in the present region and this causes delayed recombination.

Microscopic observations on zinc sulphide grains indicate a very heterogeneous pattern of electroluminescence in contrast to the uni-form emission under ultra-violet excitation. Some crystals remain unexcited while others show a reasonably uniform emission over the

whole grain. Others, particularly the larger sizes, and presumably imperfect, show bright spots of emission due to local inhomogeneity in the field.

The existence of these bright spots is beyond question. However, G. Destriau observed that the apparent brightness of these spots, compared to the brightness of the continuum, is considerably enhanced when the observation is made with a microscope: it is well known that the ratio of the visibility for a spot and an extended luminous surface is given by

$$\frac{V_{spot}}{V_{surface}} = G^2$$

where G is the microscope magnification. To see the continuous background emission G must be less than 100, otherwise only bright spots are observed.

P. Goldberg (1960) has described experiments with the electron microscope. Electroluminescent zinc sulphides show, quite systematically, 'etch pits' indicative of inhomogeneity (possibly dislocations) which gives an increase in conduction electron concentrations, the density of these pits being 10 to 100 times higher than in non-electroluminescent specimens. This is perhaps the first observation of any systematic difference between electroluminescent and non-electroluminescent zinc sulphides.

Techniques for improvement of electroluminescent phosphors. To obtain good electroluminescent zinc sulphide good crystallization is necessary. The crystals must have donors for generation of the accelerated electrons but few traps. Phosphors showing a good 'Destriau' effect usually show little phosphorescence.

An electroluminescent zinc sulphide can be made by the addition of donor levels or creation of potential barriers and regions of high field strength. Thus Destriau and Saddy refired zinc sulphide in an oxidizing atmosphere or with an admixture of zinc oxide, the latter giving relatively shallow donor levels. Lehmann has described the preparation of electroluminescent cells by mixing a non-electroluminescent zinc sulphide with metal particles or a semi-conductor such as Cu_2S.

The optimum concentrations of luminescence activators for electroluminescent specimens are higher than for photoluminescence. In view of the low probability of the impact ionization process, this would be expected. For ZnS(Cu) phosphors the optimum concentration

of copper for photoluminescence is about 2×10^{-4} g Cu per g ZnS
(A. Guntz), while optimum concentrations for electroluminescence
are of the order of 10^{-3} g Cu per g ZnS. The content of copper is
limited by the effect of the higher concentrations in producing a grey
powder and also by the fact that the copper will not enter the crystal
lattice. Refiring of zinc sulphide with copper added is a 'formation'
process sometimes used.

H. Froelich has shown that 'sensitization' for electroluminescence
can be produced by a second activator impurity, e.g. copper can be
included in ZnS(Mn). The latter can be excited without copper pre-
sent but needs a higher threshold field (see Fig. IX.3). ZnS(Mn)
sensitized with copper can be excited by quite low fields and the emis-
sion bands of manganese and of copper appear at the same time if
the concentration of manganese is small. At high Mn concentrations
only the manganese emission band occurs. J. Mattler and T. Ceva
have found some ZnS(Cu, Mn) phosphors to show the following
effects as the applied field is increased: at low voltages the intensity
of the manganese band rises slowly, then reaches a critical point, after
which it rises rapidly with the field. At low voltages the excitation is
probably due to the sensitizer, but at higher voltages direct excitation
occurs. It is doubtful whether associated Cu(Mn) pairs occur; the
most likely process is hole migration from the copper to the man-
ganese centres, thus emptying the latter in readiness for recombina-
tion.

Some organic materials show light emission in an applied field
(e.g. gonacrin and acridin orange) (A. Bernanose *et al.*). In many
ways the behaviour is like that in the Destriau effect. The brightness-
voltage relation is of exponential form ($e^{-B/V}$) and the brightness
waves lead the voltage oscillations, and so on. Reference should be
made to the publications of Bernanose and also to the writer's article
'Theories of Electroluminescence'.

II. ELECTROLUMINESCENCE DUE TO CHARGE CARRIER INJECTION

Injection of charge into a crystal can give rise to light emission but
differing in characteristics from those of 'intrinsic' electrolumin-
escence as follows:

(*a*) The effect is observed for direct current flow and persists for as

long as the current flows. In the Destriau effect build-up of the internal field (polarization) causes the emission to fall to zero.

(*b*) The light intensity is proportional to the current.

Electroluminescence due to charge injection arises from different mechanisms from those of the 'intrinsic' effect.

In one group of phenomena an injection occurs from an electrode into the crystal, e.g. electrons in a surface barrier with a strong applied field. The electrons are accelerated and excite luminescence centres as in the intrinsic case. Only the source of electrons is differ-
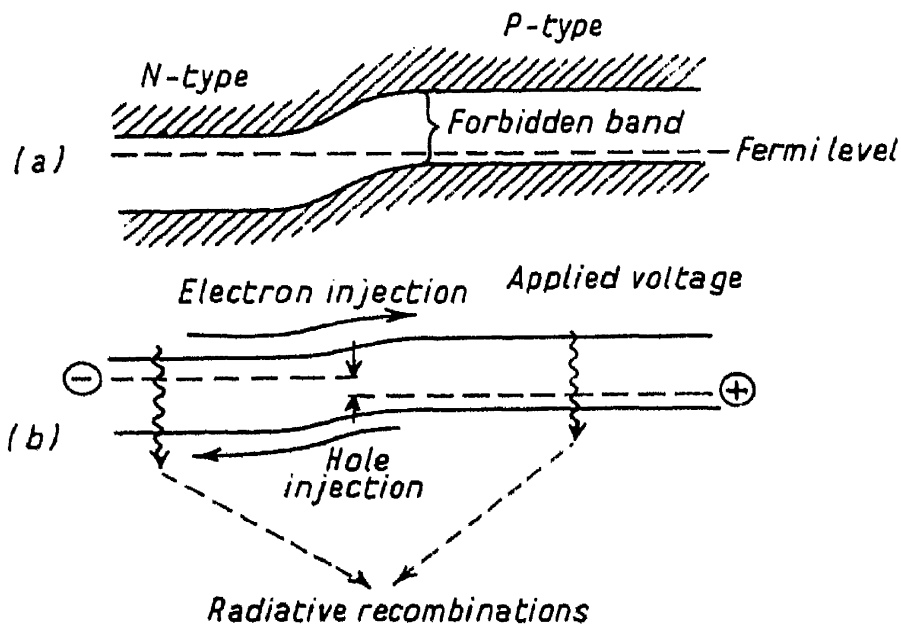
Fig. IX.13 *Energy-band diagram for a P–N junction*

(*a*) *without applied field*

(*b*) *field applied in forward direction: injection of minority carriers inferred from radiative recombination (Lehovec, Accardo and Jamgochian)*

ent. Such effects can be observed in single crystals of suitably activated zinc sulphide, or in thin films, in contact with electrodes.

In the second group light emission occurs at a P–N junction (Fig. IX.13). If operated in the forward direction electrons from the N-type material pass into the P-type and find empty centres or recombine directly with positive holes having suffered no acceleration.

If the junction is operated in the reverse or 'blocking' direction a high-potential gradient appears at the junction and carrier acceleration can occur. Completely different effects from those of the previous group occur. However, both groups show the characteristic behaviour described in (*a*) and (*b*) above.

1. Electroluminescence in single crystals or thin films of zinc sulphide between electrodes in contact with them

The first investigations were made by Piper and Williams (1952). In addition to the 'intrinsic' electroluminescence of normal type with brightness wave leading the voltage, another brightness wave in phase with the applied voltage was found (see Fig. IX.14).

The emission spectra are the same in each case but the in-phase component occurs at higher voltages and rises more rapidly with voltage than the out-of-phase component. Frankl has shown that the brightness of the in-phase emission is proportional to the current
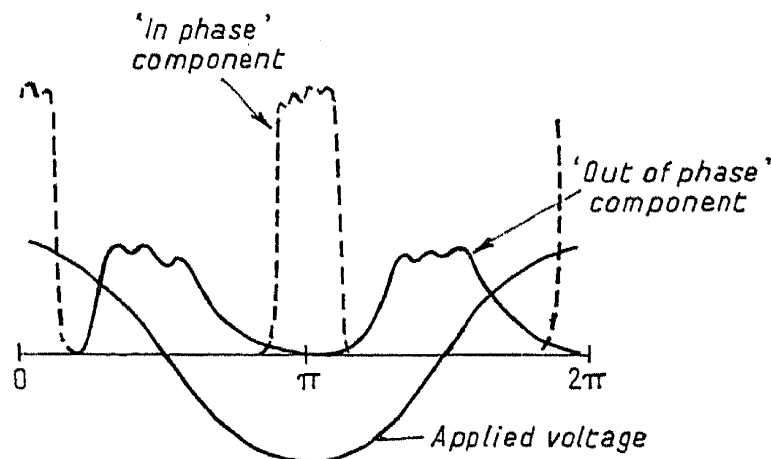
Fig. IX.14 *Out-of-phase and in-phase components of electroluminescence in relation to applied field* (*Piper and Williams*)

flowing. It most likely arises from field emission at the cathode followed by the usual processes of electroluminescence.† It has been observed in ZnS(Cu) (green and blue emission) and in ZnS(Mn), &c. Such effects can be obtained in powder-type electroluminescent cells when these have only a small proportion of binder dielectric (cf. Fig. IX.1).

Electroluminescence at low fields. Using thin films, Thornton (1959) has obtained electroluminescence from ZnS(Cu) with an applied voltage of only 1·5 V, that is, less than the mean energy of the emitted photons (2·6 eV). This is rather like the excitation of cathodoluminescence by low-energy electrons (see page 292). In order to explain this effect the nature of the electrode and its work function must be

† We might call this effect an *injection-controlled electroluminescence* (in the same way as Cusano and Williams referred to photo-electroluminescence as radiation-controlled electroluminescence).

known; perhaps there is a positive hole injection which empties the emission centres or the electrons penetrate the sulphide with enough energy to excite the centres. Whatever the mechanism, it seems unlikely that the electrons are accelerated in the sulphide.

2. Electroluminescence of cadmium sulphide in weak applied fields

Böer and Kummel and also Diemer have observed electroluminescence in cadmium sulphide at fields near to breakdown values. R. W. Smith observed emission in unactivated cadmium sulphide having indium electrodes, the field in the crystal being less than 1,000 V/cm. At room temperature band-to-band recombination of electrons and holes occurs and at liquid air temperature the Ewles–Kröger type of
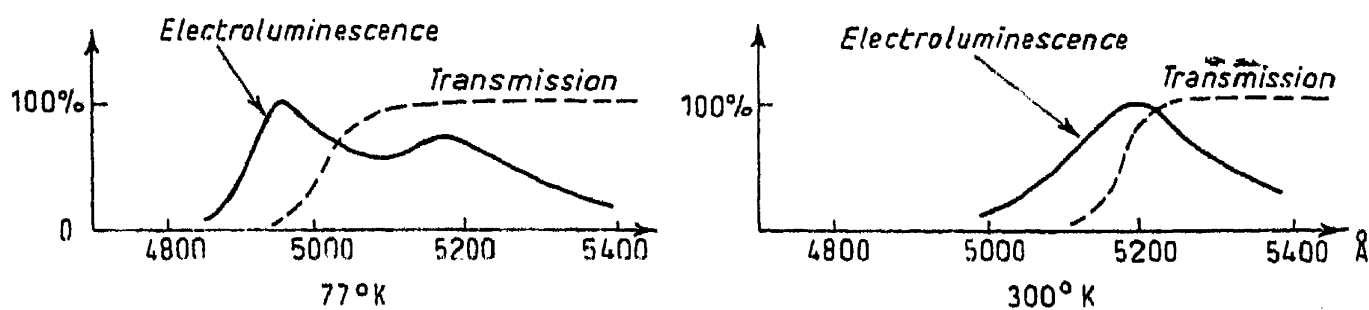
Fig. IX.15 *Emission spectrum for electron-hole recombination in cadmium sulphide (R. W. Smith)*

At 77°K band-to-band recombination (near absorption edge) and Ewles–Kröger luminescence (peak at longer wavelengths) are observed

At 300°K the Ewles–Kröger emission is quenched and only band-to-band recombination is seen

emission also appears. Indium provides an ohmic contact so that electrons can be injected at the cathode (A. Rose). Smith also assumes that certain 'formed' spots or points at the anode can give positive hole injection and so luminescence arises from electron-hole recombination in the volume of the crystal. At the anode points there are pockets of yellow luminescence and in these regions the field is high. Smith found that the intensity of the green emission was proportional to the current flowing and that the 'brightness waves' were in phase with the applied field.

3. Electroluminescence of silicon carbide

Luminous effects in rectifiers made of silicon carbide have been much studied. The first investigations were those of O. Lossew (1928–40).

The usual arrangement is a crystal of carborundum provided with a point-plane electrode system (cat's whisker). In other systems two plane electrodes have been used. Lossew found that when a voltage was applied in the reverse direction a 'Luminescence type I' appeared as luminous points near to the cat's whisker, but for the opposite or forward direction case a 'Luminescence type II' appeared in an extensive region of the crystal. The type I emission is attributed to field emission effects at the point contact and it is not seen when plane electrodes are used. Type II emission is due to the phenomenon of charge injection at a junction (Lehovec, Accardo and Jamgochian). It is only found when the crystal has a surface layer of different properties from those of its volume. For example, in a P-type crystal with an N-type surface the type II luminescence appears when the junction is biased in the forward direction (Fig. IX.13), that is, when the N-type surface is negative.

Lehovec, Accardo and Jamgochian have shown that above a certain threshold current the luminescence L is proportional to the incremental current:

$$L = a(I-I_0)$$

The 'brightness waves' are in phase with the current (G. and D. Curie).

Fig. IX.16 *Brightness waves for a SiC rectifier (G. and D. Curie)*
N.B. No out-of-phase component

For a long time the structure of silicon carbide has been little understood because of the large fractions of impurities usually present in the crystal. Slowly it has been unravelled, mainly due to the work of Kröger and Lely (Garmisch, 1956).

In many ways silicon carbide resembles zinc sulphide. The more common form is hexagonal with an optical absorption edge at 4,200 Å (2·95 eV) at room temperature.† When pure, the hexagonal crystals are colourless. They are obtained by sublimation at a

† The energy-band gap is 2·86 eV, but the absorption limit corresponds to a non-vertical transition in the band model with emission of a phonon of 0·09 eV energy (Choyke and Patrick, 1957).

very high temperature (2,500°–2,600°C). At lower temperatures ($T < 2,200°$C) a cubic form is obtained with absorption edge at 4,400 Å at room temperature, giving the crystals a yellowish colour.

Silicon and carbon both occur in group IV of the periodic table. The elements of group V, nitrogen and phosphorus, produce donor levels, those of group III, aluminium and boron, produce acceptor levels. Hexagonal SiC crystals are coloured green by nitrogen and phosphorus and blue by aluminium and boron.

Luminescence emission bands have been found in the blue and green regions and are attributed to associated donor-acceptor pairs, and in the orange region due to excess of nitrogen. For the earlier crystals investigated the preparation was not controlled carefully and gave either wholly type P or type N crystals, or samples with surface junctions. Now such junctions have been deliberately produced and have made an accurate study of electroluminescence processes possible (L. Patrick and W. J. Choyke). They involve partly a band-to-band recombination of electrons and holes and partly recombinations inimpurity centres.

Recently, intrinsic electroluminescence has been observed in silicon carbide by J. Weizburg (1960). A crystal showing the above effects when arranged as a rectifier was placed in a field of 10^6 V/cm and insulated from one electrode by a sheet of mica so that no charge injection could take place. The field was intense enough to ionize the surface donor levels and to accelerate the conduction electrons to produce electroluminescence.

4. Luminescence in electrolysis

During electrolytic oxidation of various metals luminescence is sometimes observed, particularly for aluminium electrodes.† For d.c. conditions emission occurs at the metal acting as anode and occurs in a thin insulating oxide layer in which the field is nearly 10^7 V/cm, which corresponds to a potential different of 100 V across 10^{-5} cm. Acceleration of electrons and excitation of centres occur, the emission being characteristic of impurities in the alumina layer. Often it is yellow-orange and due to manganese impurity.

The emission intensity is proportional to the current (I) and van Geel has shown that it increases with the oxide layer thickness (d) in the following way:

$$L = aI(e^{bd} - 1)$$

---

† Emission has also been found for Zr, Zn, Ta, Mg and W electrodes.

where a and b are constants. This indicates the occurrence of electron avalanches. An initial electron produces e^{bx} electrons over the path length x and so for the total thickness

$$L \propto \int_0^d e^{bx} \, dx \propto (e^{bd}-1)$$

In an alternating field scintillations occur when the aluminium is either anode or cathode. van Geel points out that there are many ways of explaining these scintillations and that different effects occur according to the nature and concentration of the impurities present. When the aluminium is the anode field emission effects can be assumed, but when acting as cathode it might be assumed that the thin oxide layer produced in the preceding half-cycle is not homogeneous and consists of an N-type region near to the electrode and a P-type region adjacent to the electrolyte.

G. and D. Curie have found that the 'brightness waves' are in phase with the applied field. The oxide layer was so thin that no luminescence was visible under ultra-violet radiation or cathode-ray excitation. With thick layers van Geel has found an appreciable phase shift for the emission relative to the field in the leading direction.

5. Infra-red electroluminescence in germanium

Although germanium has been the subject of so many precise investigations compared with the more usual luminescent solids, it is in this solid that so complex and various a collection of phenomena is found. We have already briefly described the electron-hole, band-to-band recombination emission (Chapter IV, §II) obtained by injection of electrons into a P-type region or holes into an N-type region (Haynes and Briggs, R. Newman). These workers used P–N junctions, but injection can also be produced at metal contacts. The recombination is usually of an indirect kind (simultaneous emission of photon and phonon). At room temperature the emission maximum is at 0·68 eV (about 1·8 μ): at liquid air temperature it is at about 0·72 eV (about 1·7 μ), which corresponds to the shift in the band gap with temperature.

The lowest minimum of the conduction band corresponds to the Brillouin zone edge and electron-hole recombination (with $k = 0$) is only possible by an indirect transition (see Fig. IV.2). However, there is a second minimum at $k = 0$. When the temperature is high enough to give some electrons at this minimum, then direct recombination

occurs with peak emission at about 0·81 eV (1·5 μ). The intensity of this second band rises with temperature and involves an activation energy of 0·16 eV (see page 84).

Recombination via impurity centres is generally non-radiative in germanium (so-called deathnium centres). Band-to-band recombination emission is only observed for high currents (up to 1 amp) and specimens seem to have few non-radiative centres. Thus bimolecular recombination predominates. However, certain centres give radiative recombination, e.g. an electron is captured in an empty centre and then the centre is refilled by a hole and at least one of these transi-
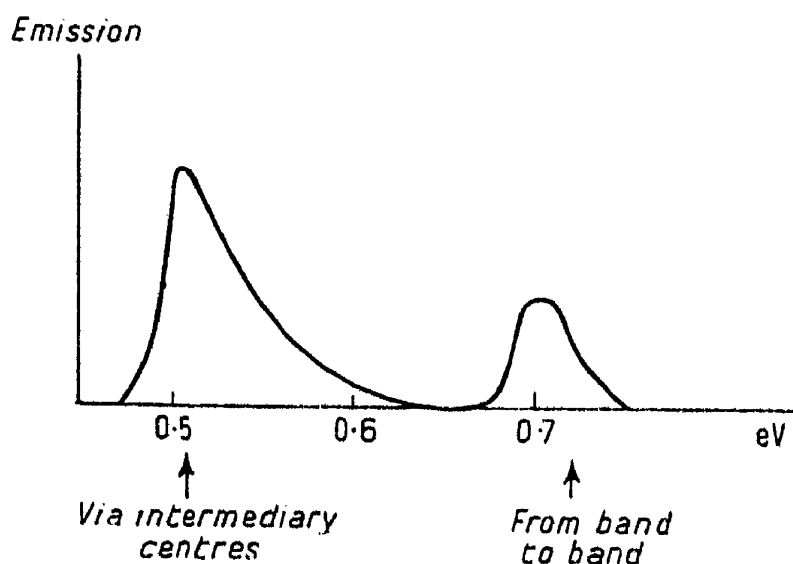
Fig. IX.17 *Radiative recombination in germanium with dislocations functioning as centres* (*C. Benoit à la Guillaume*) *Spectral distribution measured at 95°K*

tions may be made with photon emission. This is so for centres located on dislocations (C. Benoit à la Guillaume) which give a group of bands at about 0·5 eV (2·5 μ) (see Fig. IX.17). It is also the case for copper in germanium (see page 126). An electron and a hole fall into this centre and then make a radiative recombination giving an emission at 0·6 eV (2·1 μ).

We might ask why a band-to-band recombination which is bimolecular leads to an emission intensity proportional to the current and not to its square. Now the rate of recombination is proportional to the product of electron (n) and hole (p) densities:

$$R = R_i \frac{np}{n_i^2}$$

R_i being the recombination rate and n_i the carrier density in intrinsic germanium for which $n = p = n_i$.

If electrons are injected into strongly 'doped' crystals the hole density is essentially constant and np (second-order kinetics) is sensibly proportional to n (first-order kinetics result). Injection into intrinsic material also gives emission proportional to the current, though with some deviations at high current densities. Optical absorption studies show that a state is reached in which the product np is proportional to the current (R. Newman).

The above will apply when band-to-band recombination predominates, but when recombination via centres is the main process
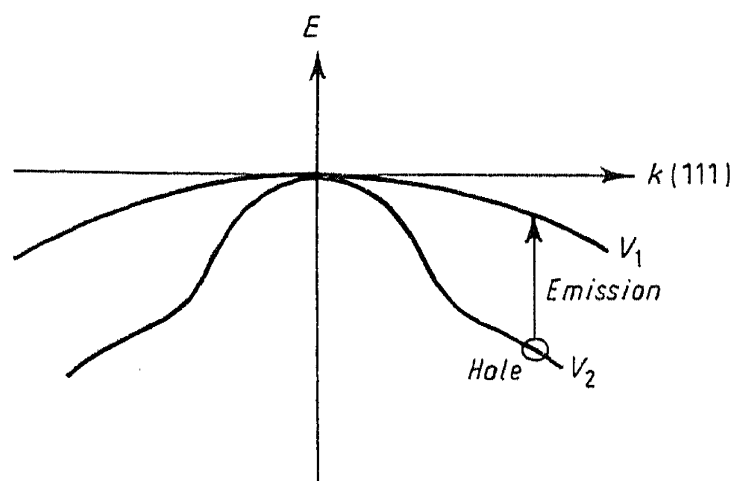
Fig. IX.18 *Structure of valence band maximum in germanium. The jump of a hole from the band V_2 (light holes) to the band V_1 (heavy holes) occurs with infra-red emission*

(Benoit) and there is competition between the two processes, the intensity of the total luminescence L is proportional to the current: $L = kI$. However, if L_1 is the intensity of the band-to-band emission and L_2 that for recombination in centres, then

$$L_1 = aI^2 \qquad \text{but} \qquad L_2 = kI - aI^2$$

Luminous effects due to 'hot' holes in germanium. P. Aigrain and C. Benoit à la Guillaume have shown that it is relatively easy to accelerate holes of small effective mass in germanium (see Fig. IX.18). The apparatus used was described in Chapter IV (Fig. IV.4), a point contact giving hole injection into N-type germanium.

The upper valence band (V_1) with small curvature corresponds to heavy holes of mass $\approx \frac{1}{3}m_0$. The lower band (V_2), with large curvature near to $k = 0$, involves 'light' holes of about $0.04m_0$ effective mass (m_0 is mass of free electron). A field of 1,000 V/cm is sufficient to

accelerate the latter and equilibrium between the light and heavy holes is destroyed.

The light holes can thus be raised in the V_2 band to a wave number k and they can then pass over to the V_1 band with emission of radiation. The emitted photon energy is given by the distance between the bands V_1 and V_2 for the k value reached by the hole. An infra-red emission results.

The band V_2 with larger curvature near $k = 0$ than the band V_1 tends to become parallel to it at high k values. The separation for k in the (111) direction is about 0·19 eV (Kane). It is also found that acceleration in the (111) direction gives emission peaking at 0·19 eV (6·5 μ wavelength) (J. Pankove).

Pankove has studied emission from the surface of germanium (by putting an ohmic contact and an injection contact close to each other at the Weierstrass point in the arrangement of Fig. IV.4). Analogous effects to the above are observed, but the high field necessary to accelerate the light holes is provided by the inversion layer at the germanium surface.

The 'hot' holes which have been accelerated also emit thermal radiations at longer wavelengths than the above (J. Kessler).

6. Other investigations

Electroluminescence effects due to charge injection through a P–N junction or emission from field accelerated charges have been observed in

(a) III–V semi-conductors such as indium antimonide (Moss and Hawkins) or gallium arsenide;

(b) some diamonds of type II (Krautz; Wolfe and Woods);

(c) cuprous oxide Cu_2O (Frerichs and Handy).

III. ELECTROPHOTOLUMINESCENCE

1. The Gudden and Pohl effect (1920)

If an electric field is applied to certain phosphors previously excited by ultra-violet radiation, X-rays or cathode rays, &c., then a burst of light is observed. This effect has been mainly investigated in sulphide phosphors of the type ZnS(Cu) or ZnS(Mn). Gudden and Pohl used a constant applied field and this was quickly annulled by the internal field, the emission being of short duration. However, a

switching off and on of the field could produce a dozen or more successive light pulses.

In an alternating field the emission lasts long enough for the form of the 'brightness waves' to be studied (G. Destriau and J. Mattler). Their amplitude decreases rapidly while their phase difference relative to the field given by

$$\tan \phi = \frac{4\pi}{K\rho\omega}$$

tends to zero as the conductivity decreases. If the field is removed and then reapplied, no more emission is observed unless several minutes elapse between cut-off and reapplication. This effect provides an indication of the retrapping in shallower traps during the interval (J. Mattler and D. Curie).

It is usually assumed that the Gudden and Pohl effect is an emptying of traps by the applied field, while electroluminescence is a field excitation of luminescence centres.

Let us consider a simple electroluminescent effect. Electrons accelerated by the field E over a path length x can empty traps of depth:

$$W_\text{traps} < eEx$$

However, in practice very few traps are emptied in this way. The light sums obtained in the Gudden and Pohl effect are very small. The change in trap population is insignificant. Destriau has, however, found several indications of a small decrease in the parts of glow curves representing very shallow traps. This supports the basic idea of the mechanism of the Gudden and Pohl effect, but there is also a clearly indicated enhancement of the thermal glow due to deep traps (recapture process during Gudden and Pohl effect).

The light pulse can be observed several hours after excitation has been removed. It certainly cannot be associated with deep traps which did not lose their electrons during this interval. It is most likely due to an emptying of traps of very short life time which are involved in a retrapping process for electrons escaping from deep traps. This may be the reason why the effect is relatively feeble. Many sulphides which do not show the Destriau effect (excitation by field alone) exhibit the Gudden and Pohl effect.

The electric field can be applied during excitation and the emission is always more intense. The brightness can be doubled or tripled at the moment when the field is applied and there is also a light flash

when it is removed. However, these effects are superimposed on permanent quenching or stimulation of luminescence by the field (see below).

I. T. Steinberger, Braun and Alexander have shown that the Gudden and Pohl effect also occurs in sulphides which are very sensitive to infra-red radiation, e.g. SrS(Eu, Sm) (see page 195). If the phosphor is previously excited, then the light-pulse intensity is much greater if the electric field is applied during infra-red stimulation than during normal afterglow. This again shows that there is no direct effect of the field on the deep traps, but an effect on shallow traps which are being constantly replenished by retrapping of electrons from deep traps.

As for intrinsic electroluminescence, the emission occurs predominantly at places in the crystals where the field is high. This is so at low voltages, but emission probably extends throughout the crystal volume as the voltage is raised to high values.

2. Permanent quenching of luminescence in ZnS(Cu) by electric fields

For an excited ZnS(Cu) phosphor (X-ray or ultra-violet excitation) the luminescence is denoted by L_0 in absence of a field (see Fig.
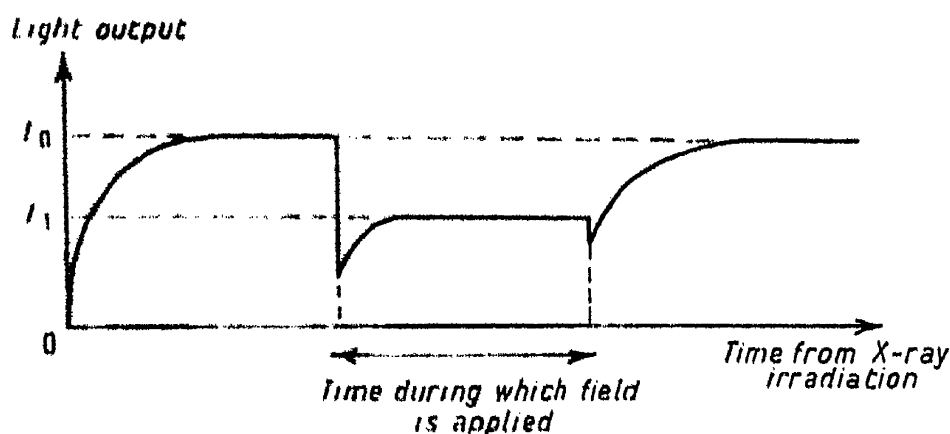
Fig. IX.19 *Quenching of luminescence due to an electric field*

IX.19). Now an alternating field E is applied during excitation; the brightness falls to L_1 and we can write

$$\tau = \frac{L_0 - L_1}{L_1}$$

where τ is the quenching factor. Destriau and Mattler have shown that curves of $\tau(E)$ at different temperatures T can be superimposed

on each other by a simple change of ordinate scale (see Fig. IX.20). This seems to show that the effect is due to a competition between radiative transitions and non-radiative transitions due to the applied
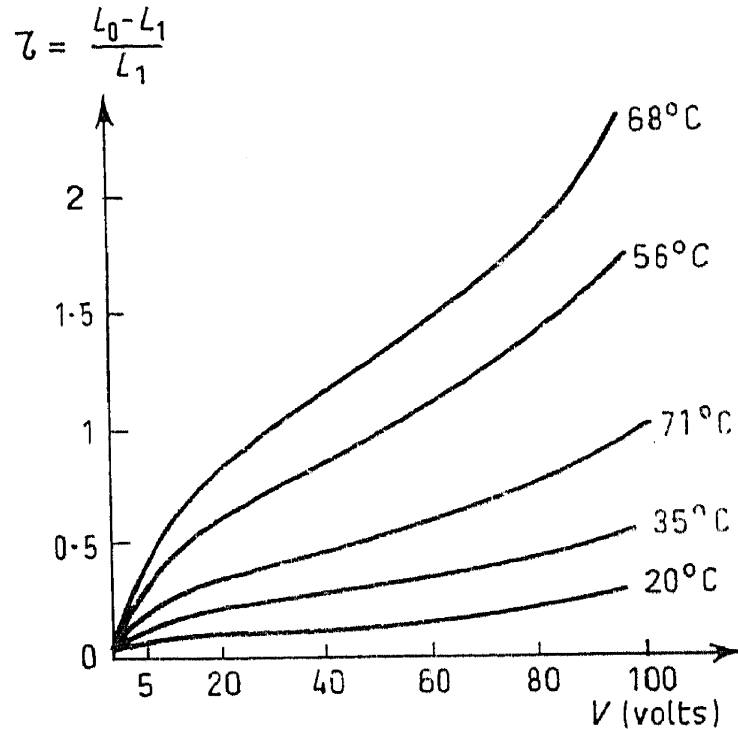
Fig. IX.20 *Variation of quenching factor τ with applied voltage V at different temperatures (G. Destriau and J. Mattler)*

field. If P_r and P_{nr} are the respective probabilities for these transitions per unit time, then we can obtain simple relations as follows:

$$L_0 \text{ (no field)} \propto \frac{P_r}{P_r + P_{nr}(T)}$$

$$L_1 \text{ (field on)} \propto \frac{P_r}{P_r + P_{nr}(T) + P_{nr}(E)}$$

The ratio

$$\tau(E) = \frac{L_0 - L_1}{L_1} = \frac{P_{nr}(E)}{P_r + P_{nr}(T)}$$

has the necessary form to explain Fig. IX.20. However, from Fig. IX.20 it is seen that in addition $P_{nr}(E)$ depends also on temperature:

$$P_{nr}(E) = f(E) . g(T)$$

and a thermal activation expression is suggested for $g(T)$ (D. Curie). For many years this quenching effect has received little attention, most of the interest being in enhancement due to electric fields (see §3) and the quenching mechanism is not yet understood. Some ana-

logy with infra-red quenching might be made. The infra red produces quenching by activation of valence-band electrons and temperature plus an electric field may do the same.

The above quenching effects have been found in microcrystalline powder-form sulphides if an alternating field is used with 'cells' constructed in the same way as for study of the Destriau effect.

Another type of extinction effect has been reported by Hershinger and others, using a CdS crystal in contact with electrodes under conditions similar to those for injection emission. When the excitation is not homogeneous, e.g. using lattice or intrinsic exciting radiation, then the

Fig. IX.21 *Quenching effect during excitation by strongly absorbed radiation (Hershinger, Daniel, Schwarz and Lasser)*

effect is observed (see Fig. IX.21). The excitation is confined to the surface and the less mobile holes remain in this region, which is then the only one with empty centres. If the field is so applied that the irradiated surface is negative (cathode), the electrons are moved away and cannot recombine with the empty centres or the holes, which gives rise to an extinction effect. The latter can be almost complete and occurs for quite reasonable field strengths (d.c.).

3. Permanent enhancement of luminescence by electric fields

The theory of electroluminescence would suggest this possibility. If a phosphor has insufficient donor levels to provide conduction electrons in the absence of photo-excitation, then it will show very weak electroluminescence. However, if the phosphor is excited to give a large number of conduction electrons, then field application during excitation will enhance the number of excited centres. This might be called radiation-controlled electroluminescence or photo-electroluminescence (Williams and Cusano).

The first kind of enhancement effect was found by G. Destriau and M. Destriau (1954). They used zinc sulphide powders immersed in a dielectric and with an alternating applied field, the arrangement being similar to that of an electroluminescent 'cell'. X-ray excitation was

used and phosphors of the type ZnS(Mn), ZnS–CdS(Mn), ZnS–CdS (Mn, X) where X is gold or cobalt. However, these effects are not explicable by the above mechanisms. They occur for quite weak fields for which electron acceleration would be rather unlikely. In any case
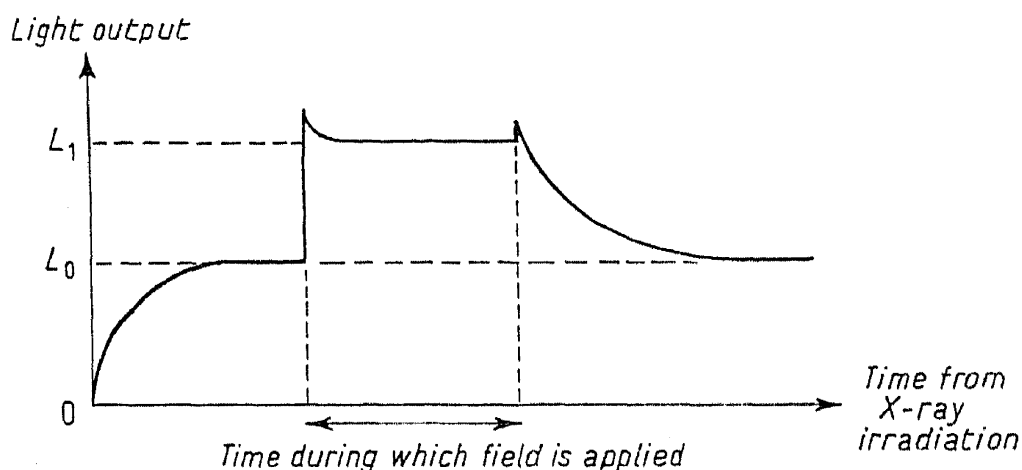
Fig. IX.22 *Enhancement of luminescence by*
an electric field

the curve for the variation of enhancement with applied voltage V is very different from the exponential relation for electroluminescence due to impact excitation. The enhancement shows a saturation which is similar to that for the current through an ionization chamber as
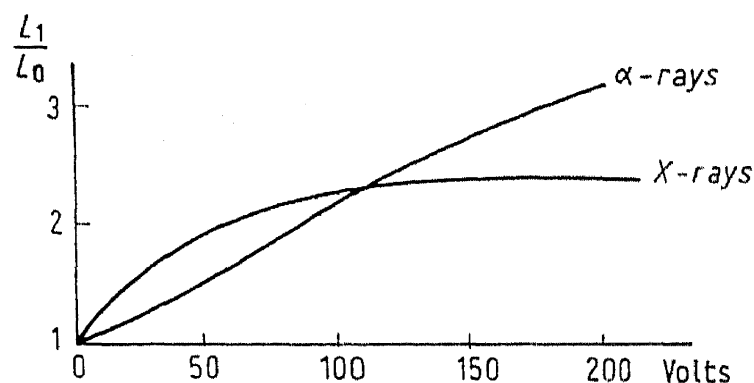
Fig. IX.23 *Variation of enhancement ratio with applied*
voltage (G. Destriau and J. Mattler)
When ionization density is high (α particles) the trend
towards saturation only occurs at very high voltages

a function of field. We may assume that a migration of charge carriers (holes and electrons) occurs due to the field, without acceleration, and these can then 'excite' centres which would not be available in the absence of a field.

Using a notation similar to that adopted previously (see §2) let P_r be the radiative transition probability and P_{nr} be the non-radiative probability. In the present instance P_{nr} is not affected much by the field (quenching effect negligible in the particular phosphors), but the latter introduces an additional radiative emission probability $P_r(E)$. We might assume P_r to depend on the number of centres excited by X-rays with the field absent and $P_r(E)$ proportional to the number of extra centres capable of being excited by the charge carriers when the field is applied. The luminescence L is then given by

$$L_0 \text{ (no field)} \propto \frac{P_r}{P_r + P_{nr}}$$

$$L_1 \text{ (field on)} \propto \frac{P_r + P_r(E)}{P_r + P_r(E) + P_{nr}}$$

The enhancement ratio ρ is given by L_1/L_0. The maximum enhancement corresponds to an efficiency of unity and a relation can be established as follows:

$$\frac{\rho - 1}{\rho_{max} - \rho} = \frac{L_1 - L_0}{L_{1max} - L_1} = \frac{P_r(E)}{P_r + P_{nr}}$$

This relation varies with applied voltage V as a 3/2 power law (G. Destriau). The manganese centres excited by the field show the same emission as for X-ray or ultra-violet excitation.

The enhancement for a given sulphide is more intense, the greater the primary excitation. Thus an increase in contrast results from application of the field. The number of charge carriers capable of diffusing in the field is thus greater for higher excitation densities. The effect is not observed in ZnS(Cu) phosphors. When ionization of the centres occurs [and not internal excitation as for ZnS(Mn)] non-radiative recombination of electrons and holes predominates. Even with ZnS(Mn) phosphors the effect is not observed with 3,650 Å excitation, but it is found for X-ray and cathode-ray excitation (electrocathodoluminescence, P. M. Jaffe) and with α-particle excitation (J. Mattler).

The total light emission for ZnS(Mn) or ZnS–CdS(Mn) phosphors excited by α particles is enhanced by the field. However, J. Mattler and J. Messier have shown that the peak heights of the α-particle scintillations are not increased by the field. It is the weak scintillations and the background noise emission which are enhanced. For this reason the enhancement effect cannot be applied to scintillation

counters. However, it throws light on the scintillation mechanism. The intense scintillations result from excitation of all the centres along the ionization channel (see page 307) and cannot be enhanced, but the smaller scintillations and the background (perhaps from areas outside the channel) are enhanced.

Similarly for 3,650 Å excitation, no enhancement is observed but only quenching (the only likely effect since the quantum efficiency is about 100 per cent without the applied field). Gobrecht and Gumlich have shown that ZnS(Mn) shows enhancement (however feeble) under ultra-violet radiation for irradiation falling in the fundamental absorption region which indicates movement of both signs of carriers is necessary to produce the effect – the holes empty centres and electrons then fall into the centres with photon emission.

It has been shown recently that infra-red radiation produces permanent enhancement effects in the same sulphides with an analogous mechanism (F. Pingault, P. Jaszczyn).

In all the above effects marked retrapping and 'memory' effects occur, the enhancement being higher after previous infra-red irradiation or applied field.

4. Photoelectroluminescence (Williams and Cusano)

With a single crystal or thin film of ZnS(Mn), ZnS–CdS(Mn), &c., in contact with electrodes allowing charge injection (§ II.1) we obtain electroluminescence controlled by irradiation, both with d.c. and a.c. fields. The effect occurs with X-rays but is more marked under ultra-violet irradiation. The only thing in common with the effects above is that they are observed in ZnS(Mn), but in ZnS(Cu) a quenching effect occurs. (The experiments are made on sulphides in which electroluminescence is feeble without simultaneous excitation.) In ZnS(Mn) phosphors the yellow-orange band due to the manganese is enhanced, while the blue band associated with 'self-activated' zinc sulphide is quenched.

The enhancement ratios can be quite high, 100 to 500 times compared with 10–15 times, in the preceding phenomena. The variation with voltage indicates a somewhat different process (see Fig. IX.24). No effect is found at low voltages, but above a certain threshold the effect increases rapidly right up to the dielectric breakdown region. The enhancement occurs when the metal electrode acts as a cathode. In Cusano's experiments the contacts are not ohmic but rectifying.

In the absence of excitation the electron injection in the cathode region is small, but X-ray or ultra-violet excitation produces a positive space charge in this region (electrons are then shifted while holes are trapped), which produces further injection of electrons. The electrons are accelerated in the resulting intense field (100,000–300,000 V/cm) and can then excite the manganese centres.

Cusano showed that the same mechanism operates as in electroluminescence by measuring the ratio L/I of the emission intensity to
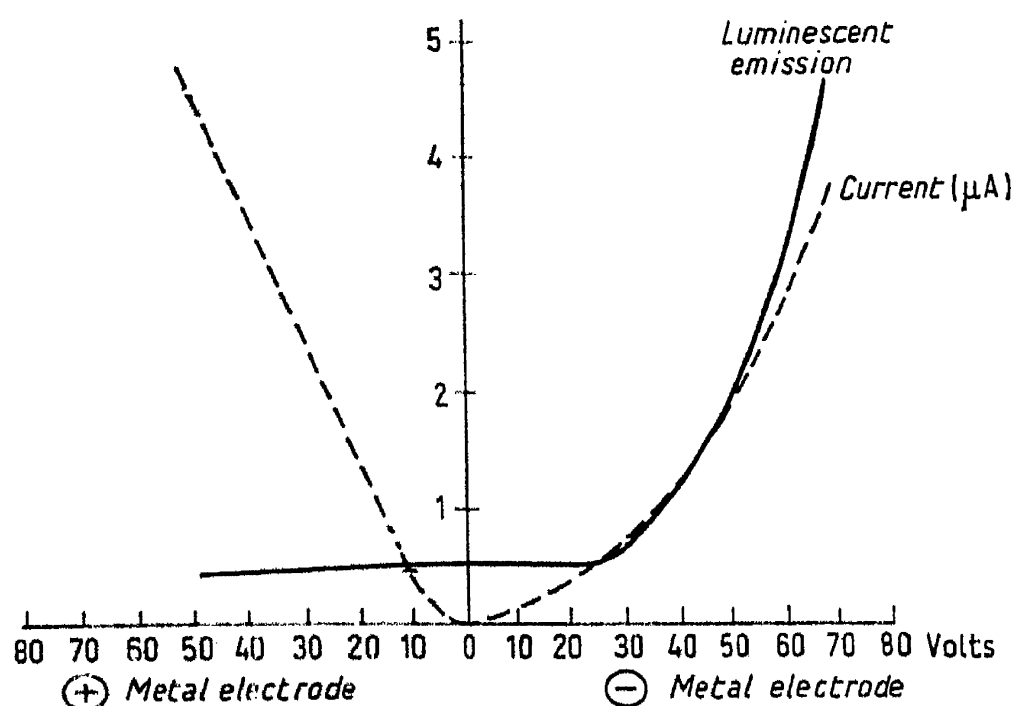
Fig. IX.24 *Photoelectroluminescence. Variation of emission and current through sulphide with applied voltage (Cusano and Williams)*

Note difference between these curves and those of Fig. IX.23. They arise from two quite different types of enhancement effects

the current density through the layer. The ratio has the same maximum value ($\approx$ 1 ft lambert/mA/cm^2) in electroluminescence and in photoelectroluminescence. One emission photon is produced per 5,000 excited electrons.

A permanent photoelectroluminescence effect is found with phosphors of the type ZnS(As), ZnS(P) and ZnS(Sb), but not by field excitation of the As, P or Sb luminescence centres. The emissions of the latter show quenching effects and it is the blue or 'self-activated' band which shows enhancement. The activators arsenic, phosphorus and antimony give centres which are ionized in the excitation process.

Their cross-sections for electron capture are very small. As a result they remain ionized when the applied field moves the electrons into an unexcited region of the crystal. The role of these activators is thus to produce a positive space charge near to the cathode to assist carrier injection, the electrons then being accelerated by the field and finally exciting the blue emitting centres (zinc vacancies).

5. Application of electroluminescence in the development of image amplifiers

Electric field enhancement of luminescence gives possibilities for image amplification. At present the best performance is obtained by a system comprising a photoconducting cell of CdS coupled to an electroluminescent panel (see Fig. IX.25).
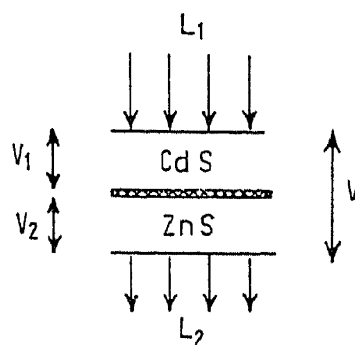
Fig. IX.25 *Schematic diagram of image amplifier comprising a photoconductive cell (CdS) and an electroluminescent cell (ZnS)*

V_1 and V_2 *are voltages applied to respective cells: V is overall voltage. At junction of the two cells is an opaque layer to prevent optical feedback from ZnS to CdS*

The principle of the amplifier is as follows:

In the absence of ambient illumination the applied voltage V is across both CdS and ZnS layers and the amount of electroluminescence emission is small. If, however, the CdS layer is illuminated, the potential across it falls due to the photoconduction and that across the ZnS layer is increased, giving a rise in brightness of the emission. The exponential change in emission with voltage is an important factor. In practice the processes are more complicated. This type of amplifier will not work with a constant applied voltage (unless the exciting light is chopped) since it uses conventional electroluminescent layers which only work with alternating fields. There are also capacity effects involved.

If C_1 is the capacity of the CdS layer and C_2 that of the ZnS layer,

Z_1 and Z_2 are their respective impedances and V_1 and V_2 their respective voltages, then we have, with V the overall voltage,

$$V = V_1 + V_2$$

$$V_2 = V\frac{Z_2}{Z_1+Z_2}$$

The admittance of the photoconductive layer is

$$\frac{1}{Z_1} = g_1 + j\omega C_1 \qquad \text{with } g_1 = b_1 L_1$$

g_1 is proportional to the intensity L_1 of the incident radiation. The admittance of the electroluminescent layer is

$$\frac{1}{Z_2} = g_2 + j\omega C_2$$

but we can neglect g_2. The emission intensity L_2 of the electroluminescent layer is given by

$$L_2 = L\omega \exp\left(-\frac{B}{\sqrt{V_2}}\right)$$

Calculations based on the above expressions by Diemer, Klasens and van Santen lead to the following:

(a) $$L_2 \propto L_1^\gamma$$

However, if L_1 becomes too large, L_2 tends towards a saturation limit.

(b) The index γ is independent of the applied field frequency, but a change in frequency shifts the region over which the relation in (a) holds. At low levels of illumination (L_1) the device can operate at low frequencies, but at higher illumination levels higher frequencies are necessary.

(c) The maximum value of the 'amplification coefficient' L_2/L_1 rises rapidly with applied voltage, but the value of γ falls. To obtain a linear relation between L_2 and L_1 high operating voltages are used. In some applications a high gamma factor is needed ($\gamma > 1$); (it can be as high as 10 to 30) and then low voltages must be used. The amplification is, however, small and several amplifiers must be used in series operation.

Fig. IX.26 *Log L_2 as a function of log L_1 (G. Diemer, H. A. Klasens and J. G. van Santen)*

Amplification factors as high as 50 or 100 have been reported.

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Cathodoluminescence, radioluminescence, scintillations. Effects of high-energy radiation on phosphorescent solids

I. CATHODOLUMINESCENCE

1. Introduction

Among the various kinds of luminescence, that excited by cathode rays would appear to have been the subject of most practical applications in recent years (e.g. cathode-ray tubes for oscilloscopes, monochrome and colour television, radar, &c.). In contrast to the large amount of experimental effort in such applications relatively little attention has been given to a better understanding of the mechanisms of the phenomenon. We shall give the main attention here to this latter. High-energy radiations such as energetic electrons, X-rays, α, β and γ rays, &c., passing through the phosphor excite or ionize the luminescence centres, this excitation or ionization being followed by visible emission from the centres.

The radiative transition process is usually independent of the mode of excitation and we obtain, for example, in cathodoluminescence the same emission bands as in photoluminescence. However, more detailed examination reveals definite shifts in the position of these bands, especially at high excitation densities. Moreover, the nature of the excitation is important in the following ways:

(a) In modifying the relative emission intensities in the different bands, this leading in certain cases (e.g. phosphors with several activators) to a change in the observed colour of luminescence. Thus in copper-activated zinc sulphide the blue band is often more intense than the green band under cathode-ray excitation than in photoluminescence; an analogous change was observed in electroluminescence (see page 270).

(b) In modifying the relative probabilities of radiative and non-

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radiative recombination, i.e. the luminescence yield or efficiency of the phosphor.

The energy conversion efficiency in cathodoluminescence lies generally between 5 and 25 per cent, while the quantum efficiency for a ZnS(Cu) phosphor excited by long wavelength ultra-violet light is near to unity.† Leverenz has shown that the thermal quenching of luminescence occurs at somewhat higher temperatures in cathodoluminescence than in photoluminescence, this being related to the higher density of excitation.

(c) In modifying the filling of electron traps, i.e. the afterglow or persistence of the phosphor when excitation ceases. The persistence is shorter after excitation by high-energy radiation than after photoexcitation (Fig. X.1).

Ultra-violet radiation will not excite luminescence unless it lies in an absorption band of the phosphor. Thus in calcium tungstate the absorption edge is at

Fig. X.1 *Comparison of decay curves for the same ZnS–CdS(Cu) phosphor after excitation by 3,650-Å (curve A) and by 6 kV-electrons (curve B)*

(*After Garlick*)

about 2,400 Å, so that luminescence is only feebly excited by the 2,537-Å radiation of a mercury lamp; addition of lead impurity enhances the excitation. It does not play the same role as, for example, copper in zinc sulphide, the luminescence in $CaWO_4$ being characteristic of the WO_4 group, but it moves the absorption limit to longer wavelengths so that absorption in the 2,537-Å region is much stronger.

In contrast, cathode rays being of small penetration power are strongly absorbed, whatever their energy. A fraction of the absorbed energy is always transferred to the luminescence centres. Many materials are luminescent under cathode rays which show no emission for long or short wavelength ultra-violet excitation. Calcium tungstate with no lead inclusion is quite well excited by cathode rays, but not by ultra-violet radiation.

† The energy conversion efficiency is only about 70 per cent since an ultra-violet photon must be absorbed to produce the smaller energy visible photon.

In radiographic screens using calcium tungstate the addition of the heavy element lead, strongly absorbing the X-rays, seems to improve the luminescence excitation.

Cathode-ray excitation is accompanied by a strong perturbation of the whole of the crystal lattice: even electrons in inner atomic shells are excited by the incident particle. The processes are much more complex than those in photo-excitation, where one considers only the valence and conduction energy bands and localized levels between these bands. Nevertheless, the efficiencies for certain zinc sulphides approach 20 to 25 per cent (Bril and Klasens) and are of the same order as those for ultra-violet excitation in the fundamental absorption band of the crystal lattice. As shown previously (see Chapter VIII), excitation involving the Riehl mechanism gives a smaller yield than that for long wavelength ultra-violet light.

TABLE X.1

Luminescence efficiencies and time constants of some cathodoluminescent phosphors (after Bril and Klasens)

(Excitation by 20-keV electrons 1 μamp/cm^2 current density: phosphor in thick layer on glass)

Phosphor	Emission colour	Luminescence efficiency		Average decay time
		Energetic efficiency (per cent)	Optical efficiency	
ZnS (10^{-4} Ag, Cl)	Blue	21	7 lumens/watt	Several components 10^{-4} to 10^{-5} sec
50 per cent ZnS, 50 per cent CdS (5×10^{-5} Ag, Cl)	Yellow	19·5	98 lumens/watt	
ZnS (10^{-5} Cu, 10^{-4} Al)	Green	23	92 lumens/watt	
ZnS (0·015 Mn)	Yellow	4	18 lumens/watt	4×10^{-4} sec
ZnO(Zn)	Green	7	25 lumens/watt	10^{-6} sec
CaWO$_4$	Blue-violet	3	2 lumens/watt	3×10^{-6} sec
MgWO$_4$	Bluish	2	5 lumens/watt	4×10^{-5} sec
CaO, MgO, SiO$_2$ (3 per cent Ti)	Blue	7	5 lumens/watt	25×10^{-6} sec
Zn$_2$SiO$_4$ (0·004 Mn)	Green	8·5	42 lumens/watt	$1·3 \times 10^{-2}$ sec
Zn$_3$(PO$_4$)$_2$ (0·03 Mn)	Red	8	13·5 lumens/watt	—
NaI (0·01 Tl)	Ultra-violet	2	—	$2·5 \times 10^{-7}$ sec to 6×10^{-8} sec

The large density of free electrons in cathode-ray excitation indicates the possibility of non-radiative recombination involving the Auger effect (Pincherle, L. Bess): instead of a simple electron-hole recombination the excitation energy is given as kinetic energy to another electron. The effect certainly exists, but it is doubtful whether it is significant here.

The principal phosphors of importance in cathodoluminescence are sulphides, selenides and tellurides of zinc and cadmium, zinc oxide, silicates and tungstates of calcium, magnesium, zinc and cadmium, and the fluorides of magnesium and zinc.

Table X.1 gives some relevant data for the more usual phosphors. The intrinsic efficiency of a phosphor is given by the ratio

$$\eta_i = \frac{\text{luminous emitted energy}}{\text{energy absorbed}}$$

in the body of the phosphor. It is clearly different from the measured screen efficiency given by the ratio

$$\eta_{\exp} = \frac{\text{luminous energy emitted}}{\text{incident energy}}$$

If the screen is sufficiently thick to absorb all the cathode rays but allowing the emission to emerge from it, then the difference between the two ratios is small (≈ 1 per cent). We give in Table X.1 the data obtained by Bril and Klasens.

2. The general laws of cathodoluminescence

(A) *Phosphor screens of type used in cathode-ray tubes (deposited as a relatively thick microcrystalline layer)*

The luminescence intensity L increases steadily with increase in electron beam current density and with the accelerating potential V for the electrons (Lenard). Although experimental conditions are not well defined in general (non-collimated beam, focused or defocused), Strange and Henderson (1946) extracted some simple relations:

$$L = f(i) \cdot (V - V_0)^q \tag{1}$$

where $f(i)$ is an essentially linear function at first, then showing a tendency to saturation for high beam current densities especially at low penetration (low electron energy). The index q is essentially independent of V and of i and remains so even where $f(i)$ ceases to be linear.

Sometimes q is unity (Lenard), this often being the case for ZnS(Mn) and Zn_2SiO_4(Mn) phosphors. More usually q is greater than unity and can reach or exceed two. It depends not only on the nature of the phosphor but also on the screen preparation, grain size and packing of the latter. V_0 is a threshold potential known as the 'dead voltage'. Actually the phosphor can be excited for $V < V_0$, but only very feebly.

(B) Cathodoluminescence due to electrons of very low energy

Since 1909 Lenard and Sealand attributed the 'dead voltage' to a superficial contamination of the phosphor by impurities and defects giving rise to non-radiative transitions. Without special precautions in preparation, V_0 can be 200–300 V, but by avoiding contamination Strange and Henderson reduced it to a few volts.

In principle an electron of zero energy can penetrate into a phosphor where its kinetic energy will be given by the electron affinity χ of
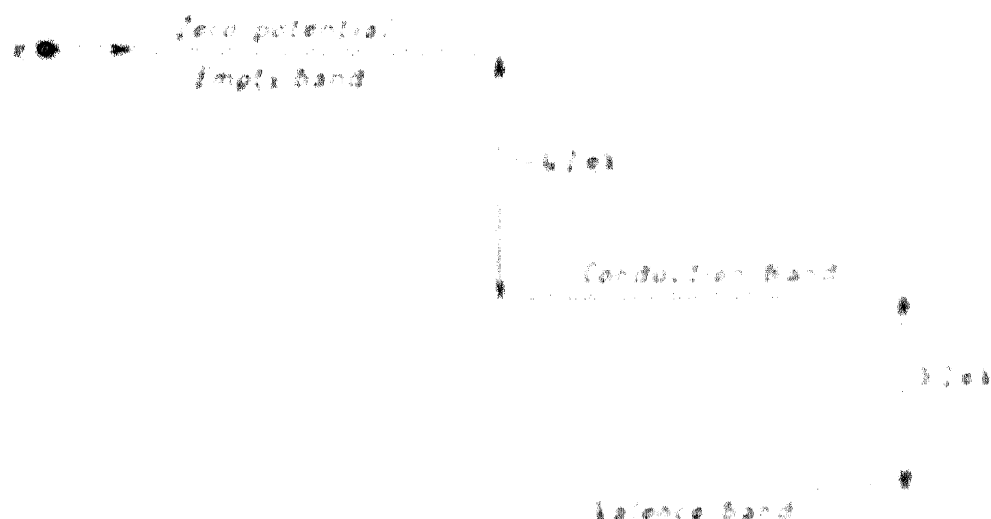
Fig. X.2 *Electron affinity χ of a crystal greater than The energy needed for centre excitation allowing a zero energy incident electron to excite emission. Numerical values are for ZnO*

(Shrader and Kaisel)

the solid (Fig. X.2). If W is the energy necessary to excite a luminescence centre, then emission will be produced if the electron energy $\epsilon > W - \chi$. If $\chi > W$, which seems to be the case in ZnS and ZnO, then zero energy electrons could produce emission. Shrader and Kaisel (1954) succeeded in observing luminescence in ZnO due to electrons with energies which, if not zero, were less than that of the emitted quantum.

In these experiments it should be noted that it is important to deposit the phosphor on a conducting base maintained at a constant potential and not on an insulating surface which will charge up and repel the incident electrons. In cathode-ray tubes the practice of aluminizing can improve the efficiency by 50 to 100 per cent.

(C) Screens in the form of a transparent film or a thin microcrystalline layer

Studer and Cusano have made cathode-ray tubes with a thin transparent layer as screen. Williams has indicated that besides their theoretical interest these screens have a much greater resolution and optical contrast than conventional powder layers and have a more well-defined geometry. Koller and Alden (1957) have studied the excitation of such a film with electrons of increasing energy.

The thickness of these films being of the order of one micron, only electrons of small energy are completely stopped in the film: a 10-keV electron with a range of $2\,\mu$ will be transmitted. Koller and Alden have shown that if the electrons are completely stopped in the film, then the index q of equation (1) above is unity and a linear response to electron energy occurs.

It should thus be asked if the various values of q are not due to the perturbations produced by the nature of the screen in conventional cathode-ray tubes: thick powder layers involve non-uniformity of excitation, occurrence of space charge between grains, light losses, &c., while the basic process is still a linear one (M. and D. Curie, 1955). Unfortunately the published experiments of Koller and Alden seem to have been confined to ZnS(Mn), i.e. specifically with manganese centres. For this material Strange and Henderson found q values of unity for powders. It would seem necessary to extend the measurements on thin films with different activators to see whether the linear behaviour is characteristic of the fundamental excitation process.

Experiments pertinent to this point of view were made by Gy. Gergely *et al.* (1959). They used thin microcrystalline layers of phosphors so that the absorption of the emitted light was negligible, but by contrast the microcrystals had an average thickness of $8\,\mu$, so that 10-keV electrons (range 2μ) were stopped within each grain. Although such experimental conditions were less satisfactory than those for the thin films of Studer and Cusano, Gergely was able to show that the

emission was sensibly linear with voltage, and moreover for a variety of specimens other than ZnS(Mn). Having corrected for 'dead voltage' effects, he showed that a simple relation applied:

$$L = \eta i V \tag{2}$$

where the efficiency η is independent of V. He gave the following values for η:

TABLE X.2

Excitation efficiencies for phosphors studied by Gergely et al.

Phosphor	η (per cent)
$Zn_2SiO_4(Mn)$	8·5
ZnS(Ag) hex.	17·8
ZnS(Ag) cub.	19·5
ZnS(Cu) hex.	14·6
ZnS(Cu) cub.	16·6

If the efficiency were equal to unity the linearity would always occur. Since this is not so, it must be assumed that a constant fraction of the absorbed energy is effective in exciting luminescence.
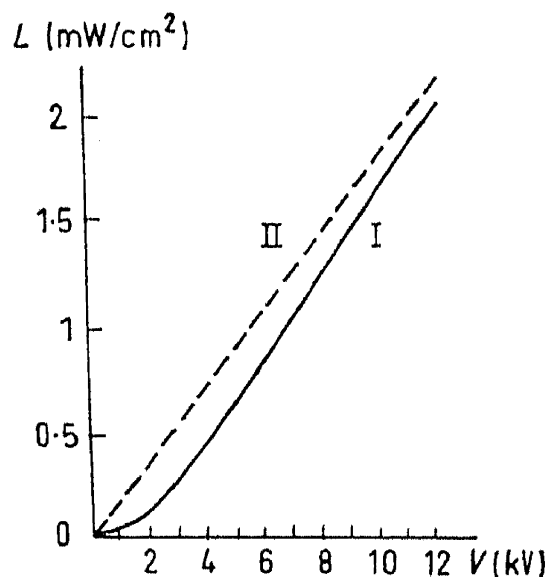
Fig. X.3 *Brightness of a ZnS(Ag) screen irradiated by a cathode-ray beam as a function of accelerating potential V* (G. Gergely)

I *Experimental curve*
II *Calculated curve allowing for energy loss in a 'dead' layer*

3. Penetration of fast electrons into matter and the excitation process

(A) Energy loss by electrons in matter

The retardation of incident electrons (primaries) occurs by detachment of electrons (secondaries) from the crystal lattice atoms or ions. In their turn these secondaries continue the excitation or ionization process. In every case and above all at low voltages (< 20 kV) some electrons emerge from the solid and an important fraction of energy is thus lost. Numerous workers have studied secondary electron emission with special reference to its energy and angular distributions which throw light on the deceleration process for the primary electrons. Reference may be made on this subject to the review articles by Garlick.

We consider here only the deceleration process. Most of the studies in this field make use of the Thomson–Whiddington law:

$$E^2 - E_x^2 = ax \tag{3}$$

where E is the energy of the incident electron and E_x is its energy after traversing a path length x into the solid, a being a constant. The total path length or range R is given by $E_x = 0$, i.e. for $x = R$, and so

$$E^2 = aR \tag{4}$$

This law is approximately valid for electrons of some tens of thousands of volts: in the energy range 40–50 keV in air.

The theory leads to the Bethe formula considering the non-relativistic form for these low energies:

$$-\frac{dE_x}{dx} = \frac{2\pi NZe^4}{E_x} \log \left[\frac{E_x}{I} \sqrt{\frac{e}{2}} \right] \tag{5}$$

where N is the number of atoms per cubic centimetre, Z their atomic number, e the electronic charge, and I a mean ionization potential for the material. If the logarithmic term is neglected (made constant), this formula gives the Thomson–Whiddington law by integration.

Bethe's calculations apply to separate atoms. The electronic system in a crystal poses particular problems. For the inner shell electrons one may preserve the Bethe assumptions, but for valence electrons the atomic wave functions must be replaced by Bloch wave functions. Calculations have been made by Dekker and van der Ziel (1952). For energies greater than about 500 eV, the assumption of Bethe's formula is justified.

The theoretical calculation of electron range can in principle be made by integrating the Bethe formula. Because of electron diffusion,

this is not possible or realistic and a semi-empirical formula has been proposed recently (C. Feldman, 1960) which is valid for energies between 1 and 10 kV.

$$R_{\text{A}} = bE^n{}_{\text{keV}} \tag{6}$$

where n is a function which increases with the atomic number of the element ($n \approx 2$ for $Z = 24$).

TABLE X.3

Values of the constants b and n of equation 6 for certain conventional phosphors

Phosphor	b	n
ZnS	63	2·4
Zn_2SiO_4	12	3·0
$CaWO_4$	17	2·7

In actual fact, n decreases slowly as the energy E increases: Katz and Penfold have proposed for aluminium ($Z = 13$ thus $n < 2$)

$$R = 113E^n \text{ with } n = 1 \cdot 265 - 0 \cdot 0954E \tag{7}$$

for $E > 0 \cdot 1$ MeV, E being expressed here in MeV and R in ångströms.

When n is greater than 2 at low energies, which is the case for the usual phosphors, then the Thomson–Whiddington law is approached at the higher energies; in the β-ray energy range one always uses the linear formulation of the range energy relation. For instance, in aluminium for $E > 2 \cdot 5$ MeV the Feather relation holds:

$$R_{\text{mg/cm}^2} = 530 \, E_{\text{MeV}} - 106$$

Measurements for phosphors in this range do not appear to be available. However, the range expressed in mg/cm² varies little with the nature of the absorber rising slowly with Z.

(B) Electron diffusion

The electrons in a cathode-ray beam of normal potential (5 to 50 keV) undergo considerable scattering in solids compared with β-rays and moreover compared with α-rays. Ehrenberg and Franks have studied the scattering of well-collimated electron beams incident on a single crystal phosphor.

An α-particle or even a β-particle incident on a phosphor excites the emission centres along a cylindrical excitation channel. The experiments of Ehrenberg and Franks show that for cathode rays this channel geometry cannot be assumed, the excitation being within a

spherical volume of secondary electrons. At low energies the surface of this sphere extends beyond the range of the primary electrons.
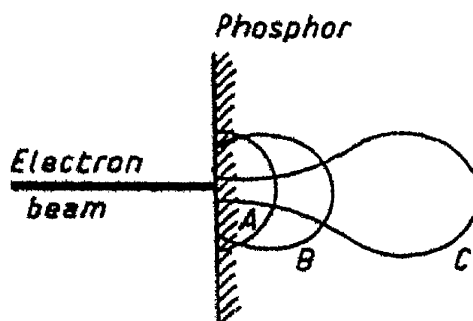
Fig. X.4 *Schematic diagram of excitation region in a crystal phosphor due to electron penetration*
(*Data of Ehrenberg and Franks used by Garlick*)
A ⟶ B ⟶ C *Increasing electron energy. At low energies the electron beam excites a spherical volume. At much higher energies a channel of excitation occurs especially when energies of MeV are reached*

(C) The excitation and emission processes

Fast electrons excite and ionize the luminescence centres. A fraction of the energy lost in the crystal lattice is finally transferred to these centres. For this a mechanism analogous to that proposed by Riehl and Schön for energy transfer can be assumed.

It must be assumed generally that the luminescence under cathode-ray excitation is due to a bimolecular recombination of conduction electrons with empty emission centres. However, the results of Strange and Henderson throw some doubt on this. For such phosphors as 'pure' ZnS, ZnS(Cu), ZnS(Ag), ZnS(Au), ZnS(Pb) they always found an exponential decay of luminescence with two components, one with a decay time of about 10^{-5} sec (α) and the other with a decay time of 0.75×10^{-4} sec (β) followed by a slow decay. The decay constants were insensitive to temperature. These data led them to propose an internal centre process without ionization.[†]

Consider for a moment the retardation of a nuclear particle in

---

[†] A sensibly exponential decay can in certain cases result from a bimolecular recombination process (if one carrier is in large excess of the other). However, the hypothesis of excitation without ionization would give the independence of the life time of excitation density and the temperature. It must be noted that Strange and Henderson expressed caution about their interpretation.

matter. One knows that it is necessary to consider the states of excitation of the atoms or molecules of the absorbant to account for the observed ionizing power: thus in air the energy lost by an α or β particle in creating one ion pair is about 35 eV, double the ionization potential, which is 17 eV for nitrogen and 15·5 eV for oxygen. Thus molecules are more likely to be excited than to be ionized. The same applies to luminescence centres in phosphors.

There is no doubt that considerable ionization is produced in the crystal lattice by fast electrons, but when the number of ion pairs created is very large compared with the activator impurity concentration (i.e. density of luminescence centres), their recombination without radiative emission seems very probable. One cannot understand the relatively high luminescence efficiencies obtained if there is not centre excitation without ionization. One cannot understand why the efficiency should be independent of the density of electron-hole pairs. We therefore suggest that for large excitation densities the luminescence arises mainly from the fraction of centres which are excited but not ionized by the primary and secondary electrons. After a certain time of decay, when the excitation density is sufficiently diminished, the electron-hole recombinations via luminescence centres will again determine the emission.

(D) Phosphor deterioration ('electron burn')

Screens of zinc and cadmium sulphide subjected to electron bombardment slowly blacken and the luminescence efficiency falls. Light and prolonged exposure in a humid atmosphere produce the same effect. Silicates and fluorides also show these 'fatigue' phenomena but to a lesser degree.

Zinc or cadmium metal is deposited in the crystal, but defects giving rise to non-radiative recombination centres are also produced. We return to this matter in section IV below. In cathode-ray tubes the phosphor may also undergo ion bombardment. This can be eliminated by use of ion traps in the tubes.

II. X-RAY EXCITATION OF PHOSPHORS

Although the primary radiation consists of photons, the excitation is due to the fast secondary electrons produced by absorption: in this respect (of excitation mechanism) X-ray excited luminescence approaches more nearly to cathodoluminescence than to photolumin-

escence, since the electron energies are of the same order of magnitude.

In the most favourable cases the quantum yield for photoluminescence is near to unity (number of photons emitted per photon absorbed). This is effectively the case for ZnS(Cu) excited by 3,650-Å radiation. For X-ray excitation the 'quantum yield' is much greater than unity.

Consider an X-ray tube running at 80 kV potential emitting X-rays of mean wavelength 0·2 Å, the radiation being incident on a calcium tungstate screen (Coltman, Ebbighausen and Altar, 1947). The emitted light has a mean wavelength of 4,400 Å. Energetically an X-ray photon could thus cause emission of 20,000 visible photons.

The intrinsic efficiency is at most 5 per cent; each X-ray photon produces 1,000 visible quanta. Such a high value can only be understood if secondary electrons are produced in the excitation. The efficiency appears to be approximately independent of the X-ray wavelength. Kallmann and Dresner (1959) have shown directly that the volume of the channel of excitation is about proportional to the energy of the incident beam. This proportionality remains the same even when the channel changes form (cf. Fig. X.4): roughly cylindrical for 35-kV X-rays, it becomes a sphere for 3·5-kV X-rays.†

In all cases, contrary to that in cathodoluminescence, the intrinsic efficiency has no more than a loose association with the light output of the screen. In practice, the screen absorbs only a small fraction of the incident X-rays, being sufficiently thick to hinder the emergence of some of the emitted light. This can be deduced from the results of Coltman, Ebbighausen and Altar:

The power of the incident X-ray beam is 714 ergs/cm²/sec, of which only 86·2 ergs/cm²/sec are absorbed in the screen, the rest being transmitted. Energy emitted as light amounts to 2·34 ergs/cm²/sec, from which a gross efficiency of 2·7 per cent is deduced. If some 55 per cent of the light actually gets out of the screen, then an intrinsic efficiency of 5 per cent is obtained.

Klasens (1947) studied the light output of fluorescent screens excited by X-rays (Fig. X.5). If N_0 is the number of incident X-ray photons, the number dN absorbed in a phosphor layer of thickness dx is

$$dN = N_0\, e^{-\mu x}.\mu\, dx$$

† A channel of excitation is associated with each of the fast secondary electrons created by the X-rays.

where μ is the absorption coefficient of the screen material for the X-rays. The luminescence emission is assumed equal to dN, which neglects saturation effects for increasing electron density.

$$dL = \eta \, dN$$

If δ is the absorption coefficient for the emitted light and if one
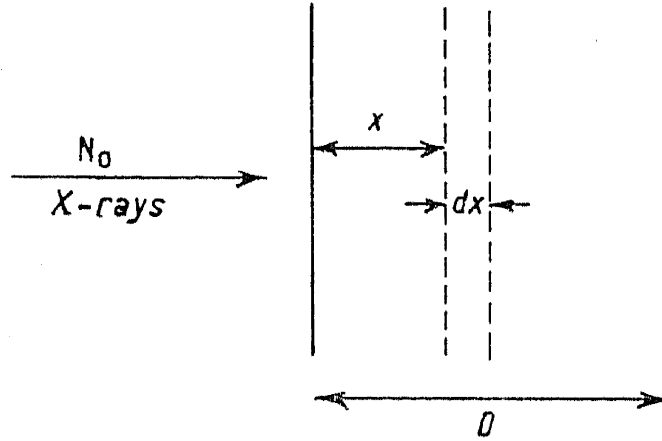
Fig. X.5 *X-rays incident on a fluorescent screen of thickness D*

looks at emission from the same side as that of the incident X-rays, the total emission is

$$L_{\text{(back of screen)}} = \int_0^D \eta \mu N_0 \, e^{-\mu x} \, e^{-\delta x} \, dx$$

$$= \frac{\eta \mu N_0}{\mu + \delta}[1 - e^{-(\mu + \delta)D}]$$

This increases tending towards saturation if D is increased indefinitely. This applies in the case of certain 'reinforcing' screens.

The emission from the other side of the screen (usual case for medical radiographic screens) is given by

$$L_{\text{(front)}} = \int_0^D \eta \mu N_0 \, e^{-\mu x} \, e^{-\delta(D-x)} \, dx$$

$$= \frac{\eta \mu N_0}{\mu - \delta}[e^{-\delta D} - e^{-\mu D}]$$

This reaches a maximum for a certain screen thickness $D = D_m$ where

$$D_m = \frac{\log \mu - \log \delta}{\mu - \delta}$$

These calculations neglect light diffusion within the screen: Klasens has shown that this can be taken care of in most cases by a modification of the coefficient δ.

In practice the efficiency of an X-ray screen is determined not only by the phosphor efficiency but also by the intensity of the X-ray absorption. For ZnS(Ag) the efficiency can reach 20 per cent and that
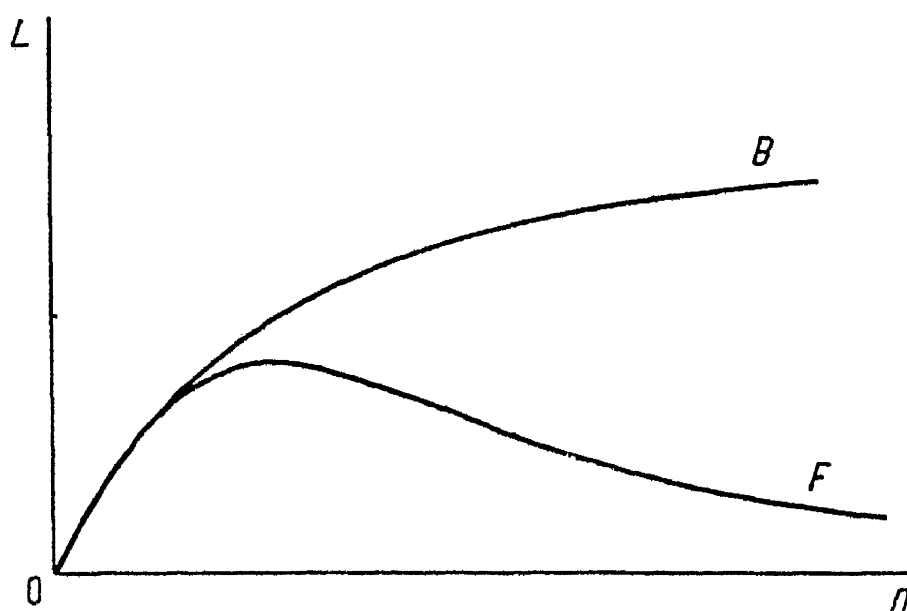
Fig. X.6 *Light L emitted by X-ray screen of increasing thickness D*

B *Viewed from back*
F *Viewed from front*

of a CaWO$_4$ phosphor 5 per cent: however, by the proximity of a heavy element (lead or tungsten), which is strongly absorbing, the emission of the tungstate screen can be made more intense. For the same reason it is more useful to use a ZnSCdS(Ag) phosphor than ZnS.

III. RADIOLUMINESCENCE – SCINTILLATIONS

1. Historical

The use of luminescence from zinc sulphide to detect radioactive rays is coincident with the history of radioactivity, e.g. the spinthariscope of W. Crookes (1903). Rutherford made a quantitative use of the scintillations produced by α particles in a zinc sulphide screen. A study of α particles scattered at different angles by nuclei made by Geiger and Marsden (1908–13) compared with Rutherford's theory led to the nuclear model of the atom, using the scintillations technique.

The subsequent development of Geiger-counter techniques and the Wilson cloud chamber led to the abandonment of this method, principally for the following reasons:

(i) the necessity for dark adaptation of the eye before measurements,

(ii) individual scintillations produced by β- or γ-rays were usually too feeble to be seen.

The modern form of the scintillation counter depends on the use of a photoelectron multiplier as light detector replacing the human eye (Curran and Baker, 1944). As the latter work remained classified until 1947 the first publications on the subject were those of Kallmann and his collaborators. In 1947 Broser and Kallmann described the use of naphthalene crystals to count β- and γ-rays. Then followed liquid and plastic scintillators (in which luminescent substances were dispersed), allowing large volume detectors for cosmic rays. Since then there has been an avalanche of developments. Thus in 1952 Garlick was able to cite 115 publications on these counters in a review article.

2. Characteristics of the main crystalline scintillators

Reference may be made to special volumes, such as those of Curran or of Birks, and more recently of D. Blanc, or to the review by Garlick, Jordan or Morton for the arrangements and special uses of the scintillation counter. We simply give here some general observations.

(A) Detection of α particles

Silver-activated zinc sulphide is one of the most efficient phosphors: several tens of thousands of photons are emitted per MeV of α-particle energy. There has been a long discussion on this subject since experiments by Riehl suggested 80 per cent conversion efficiency which was in conflict with theory. However, the work of Klasens showed that the efficiency did not exceed 20 per cent, which is quite high but no more than that of cathodoluminescence. The decay time of ZnS(Ag) is rather high, exceeding 10^{-5} sec, which prohibits rapid particle counting; this is not important for many α-particle measurements, e.g. the natural radioactive sources in common use. Zinc oxide has a decay time of 1 μsec but its efficiency is only about 20 per cent of that for zinc sulphide. Organic crystals allow of rapid counting but their yield is even less favourable for α particles (1 per cent or less).

NOTE. Reverting to ZnS, Kallmann showed that in addition to the usual decay of about 10^{-5} sec duration, there was a fast component

lasting about 10^{-7} sec due to direct excitation of emission centres without ionization (cf. page 149).

This has been measured precisely at the Atomic Energy Commission in Saclay by L. Treguier and Y. Koechlin. Exciting ZnS(Ag) by α particles, they found three components of decay:

$$\left.\begin{array}{l} \tau = 7 \times 10^{-8} \text{ sec} \\ \tau \approx 9 \times 10^{-7} \text{ sec} \end{array}\right\} \text{Blue emission only}$$

$\tau \approx 1{\cdot}3 \times 10^{-5}$ sec The α component of Strange and
Henderson (see page 297)

these being followed by a slow phosphorescence. The time constant usually measured is in general the mean† of the above, depending also on the various frequency responses of the associated circuitry. The use of suitable electronics, involving fast amplifiers, &c., allows the shortest time response of the ZnS(Ag) phosphor to be selected.

(B) Detection of β- and γ-rays

These rays, especially the γ-rays, are less absorbed than α particles:

TABLE X.4

The yields for β excitation of various scintillators

Phosphor	Maximum of emission band Å	Yield in photons per MeV	Decay time in sec
CaWO$_4$	4,400	~ 10,000	3.10^{-6}
CdWO$_4$	5,200	~ 20,000	$> 10^{-6}$
CaF$_2$	4,000	~ 5,000	$1{\cdot}5.10^{-7}$
NaI(Tl)	4,100	~ 20,000	$2{\cdot}5.10^{-7}+6.10^{-8}$
Anthracene	4,480	~ 10,000	3.10^{-8}
Stilbene	4,080	~ 6,000	$0{\cdot}6.10^{-8}$
Naphthalene	3,450	~ 1,000 (*visible*)	6.10^{-8}
Naphthalene+1 per cent anthracene	4,400	~ 5,000	4.10^{-8} †
Terphenyl in xylene	3,600	~ 2,000	4.10^{-9} ‡
Tetraphenylbutadiene in polystyrolene		~ 2,000	3.10^{-9} §

† Mixed anthracene naphthalene crystals are more transparent to their emitted radiation than pure anthracene.
‡ Liquid scintillator.   § Plastic scintillator.

† Dependent on the experimental system, values between 0·2 and tens of μseconds are possible. It seems that the duration of the scintillation produced by an α particle is some ten times shorter than that produced in cathodoluminescence measured with the same system. The proportion of the rapid components is much greater.

one therefore uses a material available in the form of large transparent crystals. The liquid scintillators are less efficient than these.

(C) Detection of cosmic rays

The energy here is so high that a poor efficiency does not matter. Liquid and plastic scintillators are particularly suitable. Plastic scintillators of 100-kg mass have been made.

(D) Detection of heavy ions, fission fragments, &c.

The response of zinc sulphide (for example) to machine-accelerated ions has been studied. Broser and Kallmann (1948) have excited ZnS(Ag) with fission fragments from U^{238}. Pulses of large size are obtained but only three times these produced by α particles from uranium. The efficiency is relatively low and effects of 'radiation damage' are considerable. The response is not a linear function of the particle energy.

(E) Detection of neutrons

A fraction of the energy lost by fast neutrons in nuclear collisions is used to excite luminescence. In hydrogenous substances the excitation occurs via the effects of recoil protons. The scintillator response is often comparable for neutrons and γ-rays, which makes it difficult to distinguish between the two.

For slow neutrons, an element such as boron may be incorporated into the phosphor. B^{10} has a large reaction cross-section (n, α) of 550 barns for thermal neutrons, the resulting α particle providing the scintillations. Lithium may also be used.

$$B^{10} + n \longrightarrow Li^7 + \alpha$$

or

$$Li^6 + n \longrightarrow H^3 + \alpha$$
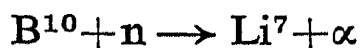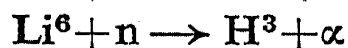
3. Linearity of response

The response of a scintillator is said to be linear when the pulse produced by each scintillation has a magnitude proportional to the energy of the incident particle (proportional counter). This is generally true when the ionization density is small: deviations from linearity occur at high ionization densities. Thus, in general, response to high-energy electrons is linear even for luminescent materials which do not show a linear response to cathode rays. Inorganic scintillators show a sensibly linear response to protons and deuterons. In

contrast to this, the response to α particles is not linear below energies of 10 to 15 MeV.

At low energies ($\leqslant 5$ MeV), the magnitude of the scintillations from silver-activated zinc sulphide is proportional to the residual
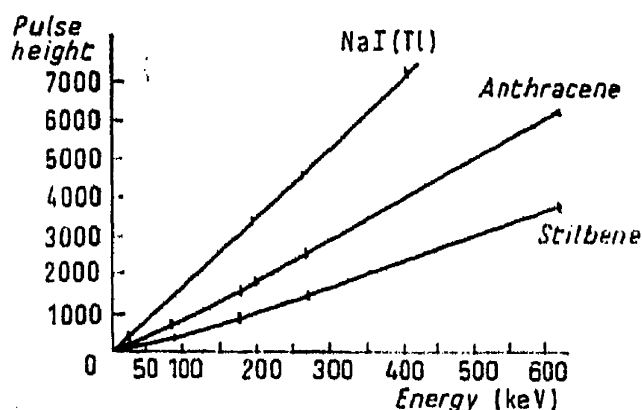
Fig. X.7 *Response of anthracene, stilbene and NaI(Tl) scintillators to electrons (Jentschke, Eby, Taylor, Remley and Kruger)*

range of the α particle (J. Anthony and G. Ambrosino). The same is true of calcium fluoride (Garlick and G. T. Wright) and also for anthracene (Birks). The simplest explanation of this is to assume that all centres are excited which lie in a channel of excitation of constant
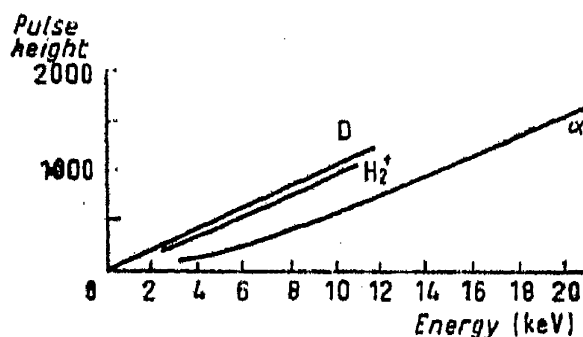
Fig. X.8 *Response of NaI(Tl) to H_2^+ ions, deuterons and α particles (Taylor, Remley, Jentschke and Kruger). Response to protons and deuterons essentially the same*

cross-section and length proportional to the residual range of the particle when it arrives at the crystal.

A short phenomenological calculation by G. T. Wright (1953) referred to by Garlick gives a sufficient account of the effects.

Let ε be the exciting energy per unit path length along the excitation channel. We assume – as was done for cathodoluminescence –

that only excitation of centres without ionization leads to an appreciable probability of luminescence emission, the intense ionization in the crystal lattice giving non-radiative recombination when the density of electron-hole pairs is much larger than that of emission centres.

The number of excited molecules or luminescence centres decays at a constant rate, with probability p for luminescence emission and q for internal quenching (non-radiative), while the ionization involves a non-radiative bimolecular recombination with a rate $\beta\varepsilon$.

G. T. Wright gives the rate of energy dissipation as follows:

$$\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} = -(p+q+\beta\varepsilon)\varepsilon$$

while the luminescence emission from an element $\mathrm{d}x$ of the excitation channel is

$$\mathrm{d}L = p\,\mathrm{d}x \int_0^\infty \varepsilon(t)\,\mathrm{d}t$$

If $\varepsilon_0 = \dfrac{\mathrm{d}E}{\mathrm{d}x}$ is the specific energy loss of the particle, then integration gives

$$\mathrm{d}L = \frac{p}{\beta}\left[1 + \frac{\beta}{p+q}\cdot\frac{\mathrm{d}E}{\mathrm{d}x}\right]\mathrm{d}x$$

The total luminescence emission during the scintillation, assuming no reabsorption of this emission, is

$$L = \int_{x=0}^{x=R}\mathrm{d}L$$

In general, this integration can only be carried out graphically. However, if $\dfrac{\mathrm{d}E}{\mathrm{d}x}$ is small, then linearity may be assumed and

$$L = \frac{p}{p+q}E_0$$

where $E_0 = \displaystyle\int_0^R \mathrm{d}E$, i.e. the energy of the incident particle. If, on the contrary, $\dfrac{\mathrm{d}E}{\mathrm{d}x}$ is large, then deviations from linearity will occur, which are found experimentally. However, the theory due to Wright does not explain the proportionality between L and R for low-energy α particles which may perhaps be associated with the saturation of the available luminescence centres in the excitation channel.

4. Size of the excitation channel, density of ionization and refilling of electron traps for the particular types of excitation

(*A*) A particle of high energy will cause considerable ionization densities in the channel of excitation. The volume of the latter can be estimated by finding the number of luminescence centres excited by each particle. As carried out by Kallmann, Spruch and Dresner, one can determine the cross-section a of the channel from the rise in luminescence excited by a constant stream of particles. Consider an area of 1 cm² with N incident particles per second. The fraction f still in the excited state at time t is given by

$$\frac{df}{dt} = Na(1-f)$$

from which we get a luminescence which rises with a time constant $\beta = Na$:

$$L = L_{max}(1 - k\,e^{-\beta t})$$

where k is a constant. The length of channel is equal to the range of the exciting charged particle.

Examples

(*a*) *β particles of about 1 MeV energy (Sr^{90})*. Range in ZnS about 1 mm such that a powder screen shows partial transmission of β particles. The diameter of channel according to Kallmann and Dresner is $\approx 1\cdot8 \times 10^{-5}$ cm. In a channel of volume 10^{-10} cm³ there will be 100,000 excited electrons, giving an ionization density of the order of 10^{15} electrons/cm³.

(*b*) *35-keV X-rays*. Each secondary electron produces an excitation channel equal to its range, i.e. $\approx 3 \times 10^{-4}$ cm. Diameter of channel $\approx 9 \times 10^{-5}$ cm. Ionization density 10^{15} to 10^{16} electrons per cm³.

(*c*) *5·3-MeV α particles (polonium)*. Range in ZnS $\approx 15\,\mu$, number of centres excited per α particle 500,000. For 10^{18} centres/cm³ (4×10^{-5} g Cu per g ZnS) the volume of channel is 5×10^{-13} cm³. Radius of channel is 10^{-5} cm, giving considerable ionization density $\approx 10^{18}$ electrons per cm³ or as much as 10^{19} in the first instant following excitation before electrons have had time to diffuse out of the channel.

(*d*) *Comparison with densities due to ultra-violet excitation*. Consider a layer of zinc sulphide emitting 10^{16} photons per sec/cm². For green light this corresponds to a luminescence of 2·5 lamberts (0·8 candle/cm²). Long wavelength ultra-violet radiation penetrates 0·1 mm. In

a layer of thickness 0·1 mm and area 1 cm² there will be 10^{16} recombinations per second, giving 10^{11} free carriers (assuming a life time of 10^{-5} sec). The free carrier density will then be $\approx 10^{13}$ electrons/cm³.

With the usual sources of excitation this value can vary between 10^{11} and 10^{14}.

(B) Fraction of filled traps

Although total filling of traps can be achieved by ultra-violet light excitation the percentage filling for particle excitation is small (≈ 1 to 5 per cent). For example, even after a very intense α-particle excitation only a very feeble phosphorescence is observed. For electron or X-ray excitation the filling of traps is a little greater than this. The diameter of the excitation channel is much smaller than the diffusion length of the electrons before trapping. This indicates that they will recombine preferentially with holes.

IV. RADIATION DAMAGE IN PHOSPHORESCENT SOLIDS

Daylight produces a blackening of zinc and more so of cadmium sulphide, attributed to freeing of metal (by breaking of atomic bonds) this being a photochemical action. The metal becomes colloidal and the damage is irreversible. The effect involves liberation of electrons into the conduction band, followed by their capture on zinc or cadmium ions. Gordon, Seitz and Quinlan (1939) give the following reaction:

$$Zn^{2+} + e^- \longrightarrow Zn^+$$
$$2Zn^+ \longrightarrow Zn^{2+} + Zn$$
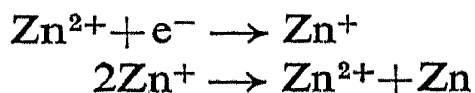
The blackening is more rapid for radiation of quantum energy $h\nu$ greater than the energy-band gap. This is why for daylight irradiation it is seen more readily in mixed ZnS(CdS) crystals with a high proportion of CdS. The effect is less marked when $h\nu$ is less than the band-gap energy and is related to localized levels, e.g. those introduced by copper impurity.

However, more effective than the phosphor composition is the influence of humidity. The electron liberation takes place within the crystals, but bond rupture occurs where the zinc sulphide is already partially dissociated and has a weaker binding energy. Blackening

is more rapid for wurtzite (hexagonal) than for blende (cubic) type crystals, the latter having greater chemical stability.

In *electroluminescence* the same process takes place with the same effect of humidity and is the principal cause of the deterioration of electroluminescent panels (Smith, Potter and Aven). If humidity is removed, the deterioration is less marked. It seems that the rotation of the sulphide grains produced by the internal electric field of the dielectric must equally lead to a lowering of luminescence efficiency. There is also perhaps a diffusion of impurities and lattice defects to the interior of the phosphor under the action of the applied electric field.

High-energy radiations also produce the above phenomenon, but this is accompanied by other effects. Electrons accelerated in a cathode-ray tube rarely have energies sufficient to produce lattice vacancies and interstitial atoms. This requires an energy of about 8·7 eV in CdS (Kulp and Kelley, 1960) and probably a higher value in ZnS (15 eV?). This corresponds to a minimum threshold energy of bombarding electrons in CdS equal to 115 keV.

When the energy exceeds this threshold value the incident electrons create centres in cadmium sulphide responsible for the edge emission at 5,200 Å and also for the red band at 7,600 Å.† These emission bands can therefore be attributed to vacancies or interstitial atoms. To specify which model applies to each centre requires a number of additional experimental data.

When the energy is less than that of the threshold, then besides the photochemical destruction of the phosphor screen, F or colour centre

Fig. X.9 *Deterioration of luminescence of various phosphors under steady cathode-ray excitation (J. Rottgardt)*

formation occurs (particularly for radiation of small penetration

† Cadmium sulphide showing ultra-violet excited emission bands before bombardment shows the same under electron excitation, but the edge emission gradually disappears.

L

depth confined to the surface layers). Hill has shown directly the existence of this effect in fluorite absorption bands occurring in the ultra-violet region. We assume, with Garlick, that these centres cause non-radiative transitions. The process does not cause such a rapid destruction of luminescence as that observed in zinc sulphide.

In cathode-ray tube screens, 'sticking' of electrons will cause a reduction of luminescence due to electrostatic repulsion of incident primary electrons, but this can be eliminated by proper aluminizing of the screen.

Heavy particles produce many defects. In the absence of information on luminescent sulphides, we give data for semi-conductors:

1 α particle of 5 MeV energy produces 100 vacancy interstitial pairs
1 H_2^+ ion of 10 keV   ,,   ,,   20   ,,   ,,   ,,
1 p   of 20 MeV   ,,   ,,   100   ,,   ,,   ,,
1 n   of 2 MeV   ,,   ,, 2,000   ,,   ,,   ,,

The luminescence efficiency thus falls with the number N of incident particles.

The case for α particles. The destruction of luminescence centres by α particles was considered in very early work. Rutherford gave a formula, based on the idea that each centre could only be excited once by an α particle, as follows:

$$\frac{L_N}{L_0} = \frac{1}{\lambda N}(1-e^{-\lambda N})$$

where λ is a constant, L_N being the luminescence after bombardment by N particles and L_0 the initial luminescence.

Currently it is assumed that α particles produce deep-lying defect traps which function as non-radiative recombination centres. Hanle and Rau (1958) give a formula for ZnS as follows:

$$\frac{L_N}{L_0} = \frac{1}{1+AN} \tag{1}$$

where A is a constant.

The formula is applicable for deuterium ions (Martin, 1957).

For CdS, Broser and Warminsky proposed a different formula:

$$\frac{L_N}{L_0} = 1-\log\left(1+\frac{a}{N}\right)^{N/a} \tag{2}$$

where a is a constant.

It appears that equation (1) is more applicable when the density of excited electrons is much larger than the activator concentration, while equation (2) applies when the latter is of the same order as the

excited electron density (in this case the bimolecular recombination of electrons and holes in the centres following ionization can be radiative, this being the assumption made by Broser and Warminsky).
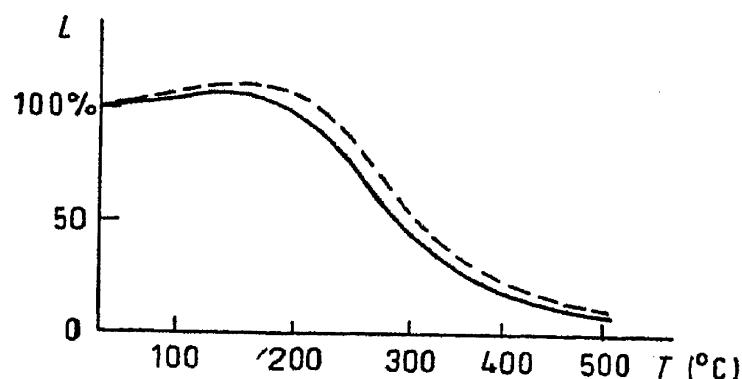
Fig. X.10 *Thermal quenching of ZnS(Cu) phosphor*
(*W. Martin*)

------ *before irradiation*
——— *after bombardment by* 10^{13} H_2^+ *ions/cm²*

The defects or traps produced by bombardment are too deep to show up in the thermoluminescence of ZnS. However, their existence is confirmed by a study of thermal quenching which occurs at lower temperatures after irradiation (see Fig. X.10). Infra-red quenching
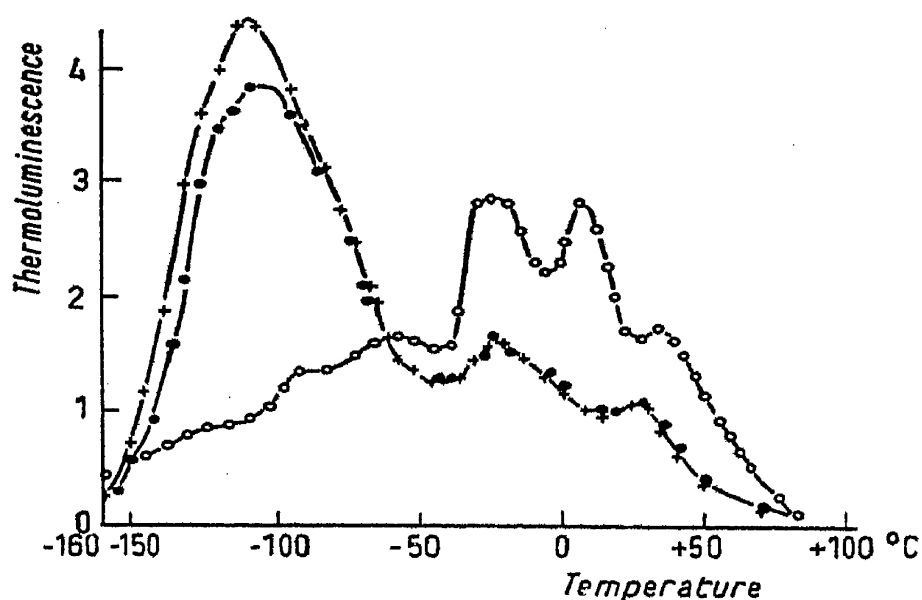
Fig. X.11 *Thermoluminescence curves of ZnS(Cu) phosphor*
(*W. Martin*)

++++ *before irradiation*
ooooooooo *after bombardment by* 10^{14} H_2^+ *ions*
●●●● *after regeneration by* 2.10^{15} *electrons*

effects are specifically enhanced while infra-red stimulation practically disappears (F. Bandow, 1956). In contrast to α-particle irradiation, that due to deuterons produces traps which are evident in thermoluminescence (W. Martin, 1957). After a bombardment by 10^{15} electrons per cm², the original thermoluminescence characteristics are restored.

This makes it doubtful whether the traps are due to ion displacements (defects or interstitials), but the effect can be well explained using the trapping model described on page 168. The irradiation of
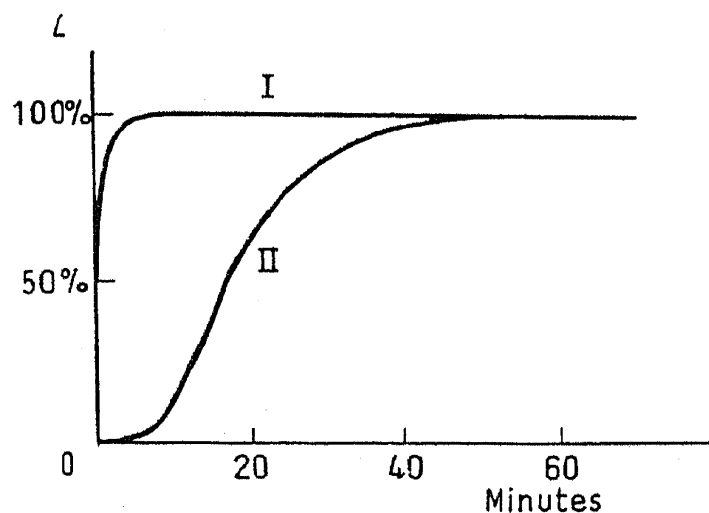
Fig. X.12 *Rise of luminescence L of a ZnS(Cu) phosphor under ultra-violet excitation*

I *Screen before neutron irradiation*

II *After 16 hours pile irradiation at Brookhaven with* $\sim 5 \cdot 8 . 10^{16}$ *neutrons per cm²*

The slower rise indicates that many more levels have to be filled (Smith and Turkevich)

ZnS by H_2^+ ions diminishes the number of traps of depth 0·28 eV attributed to the capture of electrons by discrete substitutional impurity charges with an enhancement of electrons in traps of depth $E \approx 0.5$ eV due to capture by doubly charged trap sites. In this explanation one of the two charges is provided by the incident H_2^+ ion. Protons should produce a very similar effect.

Neutron damage was studied by Smith and Turkevich. Neutrons produce a large number of deep trap effects, but these do not show in the thermoluminescence curves. However, there is an overall reduction in thermoluminescence intensity (some 'glow' peaks are more affected than others). Again, thermal quenching effects occur at lower

temperatures after irradiation. The damage can be removed by heating for a few minutes at 900°C.

Transmutations in zinc sulphide phosphors

Transmutations using α particles. The reaction

$$Cu^{63} + He^4 \longrightarrow Ga^{66} + n$$
$$\downarrow \qquad \qquad (\tau \approx 9 \cdot 2 \text{ hours})$$
$$Zn^{66} + \beta^+$$
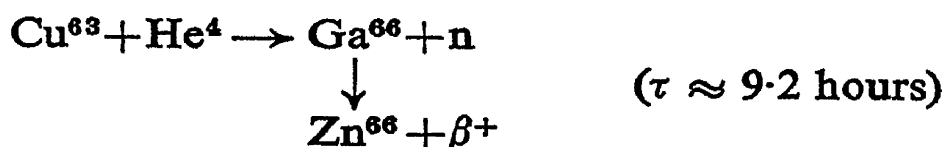
is known, but is very weak and almost unobservable for copper at impurity concentrations.

Transmutations due to neutrons have been applied by E. and M. Grillot to impurity centres in ZnS and CdS.

With silver there are two reactions:

Ag^{107} (51·35 per cent) (n, γ) Ag^{108} $(\tau = 2 \cdot 33 \text{ min}, \beta \text{ emission})$

                 (n, n) Ag^{107} $(\tau = 44 \cdot 3 \text{ sec}, \gamma \text{ emitter})$

Ag^{109} (48·6 per cent) (n, γ) Ag^{110} $(\tau = 270 \text{ days, K capture})$

           $\sigma = 1 \cdot 4 \text{ barns}$ $(\tau = 22 \text{ sec}, \beta \text{ emitter})$
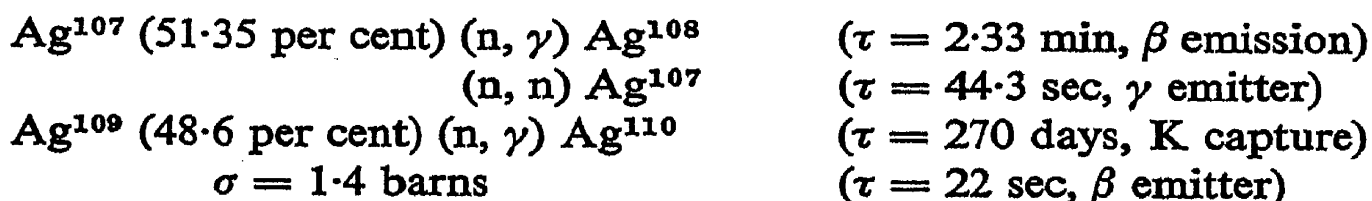
Because of the life time the 270-day decay process is used in analysis. After pile irradiation at Saclay, a silver content of 2×10^{-8} Ag/g CdS was found. It was also shown that a part of the silver tended to remain on the surface of the phosphor grains, but about 80 per cent of the silver actually diffused into the crystal lattice.

Copper detection. The following reaction is used:

Cu^{63} (n, γ) Cu^{64} $(\tau = 12 \cdot 8 \text{ hours } \beta^-, \beta^+ \text{ emission and K capture})$
$$\sigma = 2 \cdot 7 \text{ barns}$$
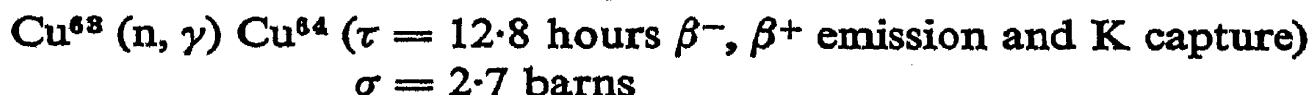
Copper may be introduced into zinc sulphide by the following reactions of the lattice zinc

$$Zn^{64} (n, p) Cu^{64} \quad \text{and}$$
$$Zn^{64} (n, \gamma) Zn^{65} \longrightarrow Cu^{65} \text{ by K capture}$$
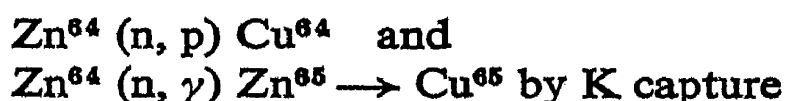
An amount of copper greater than 10^{-5} g Cu per g ZnS may be measured but not smaller concentrations. This difficulty is not found for copper in cadmium sulphide. In contrast to the case of silver, nearly all the copper is substitutional in the lattice.

Detection of chlorine

Cl^{35} (75·4 per cent) (n, γ) Cl^{36} $(\tau = 400,000 \text{ years}, \beta^- \text{ emitter})$

Cl^{37} (24·6 per cent) (n, γ) Cl^{38} $(\tau = 38 \cdot 5 \text{ min}, \beta^+ \text{ emitter and}$
$$\text{K capture})$$
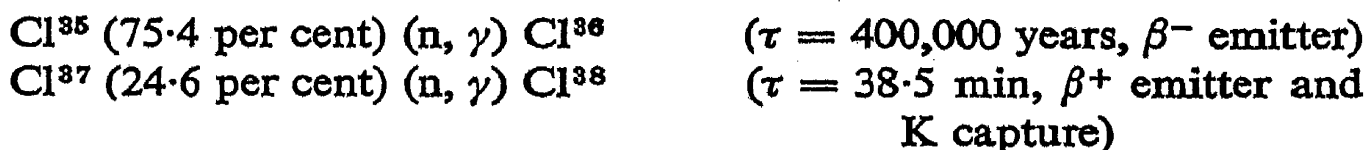
After thermal neutron irradiation of the sulphide for several hours

the chlorine can be distinguished from other radioactive isotopes with a dosage precision better than 10^{-6} cm Cl per g CdS. In practice, chlorine can be almost completely eliminated initially from the sulphide, and then more copper than chlorine (5 times) introduced at 500°: it is not essential for the chlorine ions to provide activator charge compensation for the introduction of Cu^+ ions to be possible (E. and M. Grillot).

APPENDIX I

Phosphors for monochrome and colour television

In 1957 a symposium on the problems of colour television was held in Paris. Reference may be made to the symposium publication, particularly to the contribution of H. A. Klasens and D. A. Bril.

1. *Introduction: the chromaticity diagram*

If we assume three primary colours, red (*A*), green (*B*) and blue (*C*), then any colour may be defined by three quantities, *X*, *Y* and *Z*, which represent the respective amounts of *A*, *B* and *C* which must be mixed to obtain a match to that colour. The quantities

$$x = \frac{X}{X+Y+Z}; \qquad y = \frac{Y}{X+Y+Z}; \qquad z = \frac{Z}{X+Y+Z}$$

are the trichromatic coordinates for the particular colour. They are governed by the identity

$$x+y+z = 1$$

and so specification of two of them, *x* and *y*, will define the colour.

Light sources of different spectral distributions can give the same colour sensation: in contrast to the ear the eye does not seem capable of analysing the frequency spectrum.

The choice made by Maxwell consisted of the real primary radiations:

red 0·630 μ; green 0·528 μ; blue 0·457 μ

However, it was found that it was impossible to represent all real colours without accepting in time negative values for the trichromatic coefficients.

The International Committee on Illumination took unreal primary colours determined so that negative coefficients could not occur.

These colours are defined thus:

$$\text{Red} \quad 0{\cdot}700\,\mu \begin{cases} x = 0{\cdot}73 \\ y = 0{\cdot}27 \\ z = 0 \end{cases}$$

$$\text{Green} \ 0{\cdot}546\,\mu \begin{cases} x = 0{\cdot}27 \\ y = 0{\cdot}72 \\ z = 0{\cdot}01 \end{cases}$$

$$\text{Blue} \quad 0{\cdot}4358\,\mu \begin{cases} x = 0{\cdot}17 \\ y = 0{\cdot}01 \\ z = 0{\cdot}82 \end{cases}$$

If the amounts of these three colours are given, then a simple linear
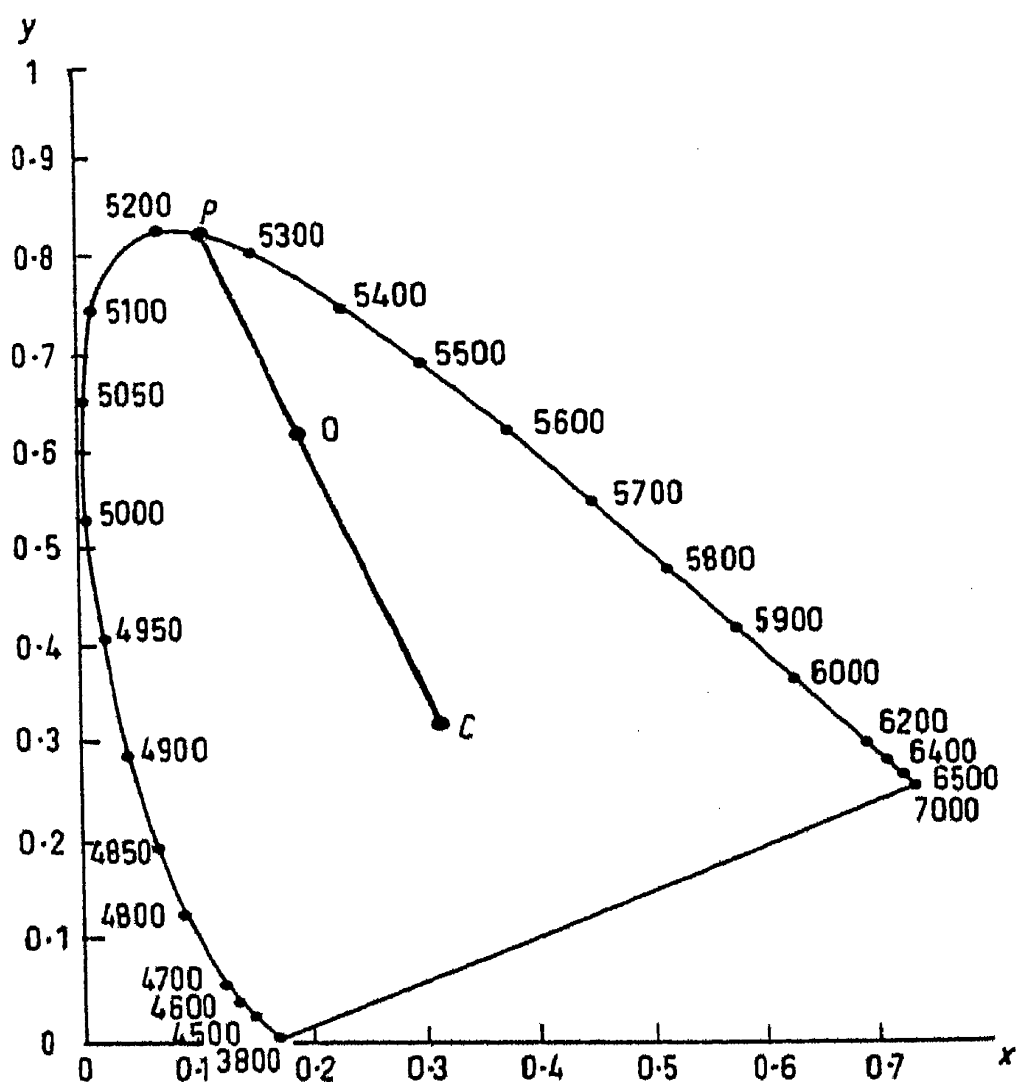
Fig. X.13 *Chromaticity diagram showing position of spectral colours and the point for 'illuminant C'*
The point O represents a ZnS(Cu) phosphor of dominant wavelength 5,240 Å and purity about 60 per cent

substitution allows the coordinates for the trichromaticity to be determined.

White light (daylight) known as illuminant C has the coordinates $x = 0.31$, $y = 0.316$.

Dominant wavelength and purity. Consider a zinc sulphide phosphor (wurtzite) with a green emission band only. It is represented on the chromaticity diagram by the point O with $x = 0.19$ and $y = 0.625$. The straight line CO cuts the position of the spectral colour at a point P which determines the *dominant wavelength*.

The colour O can be obtained by adding to the spectral colour P a certain amount of white C. The purity is defined as CO/CP.

Different zinc sulphides, activated with copper and showing pre-
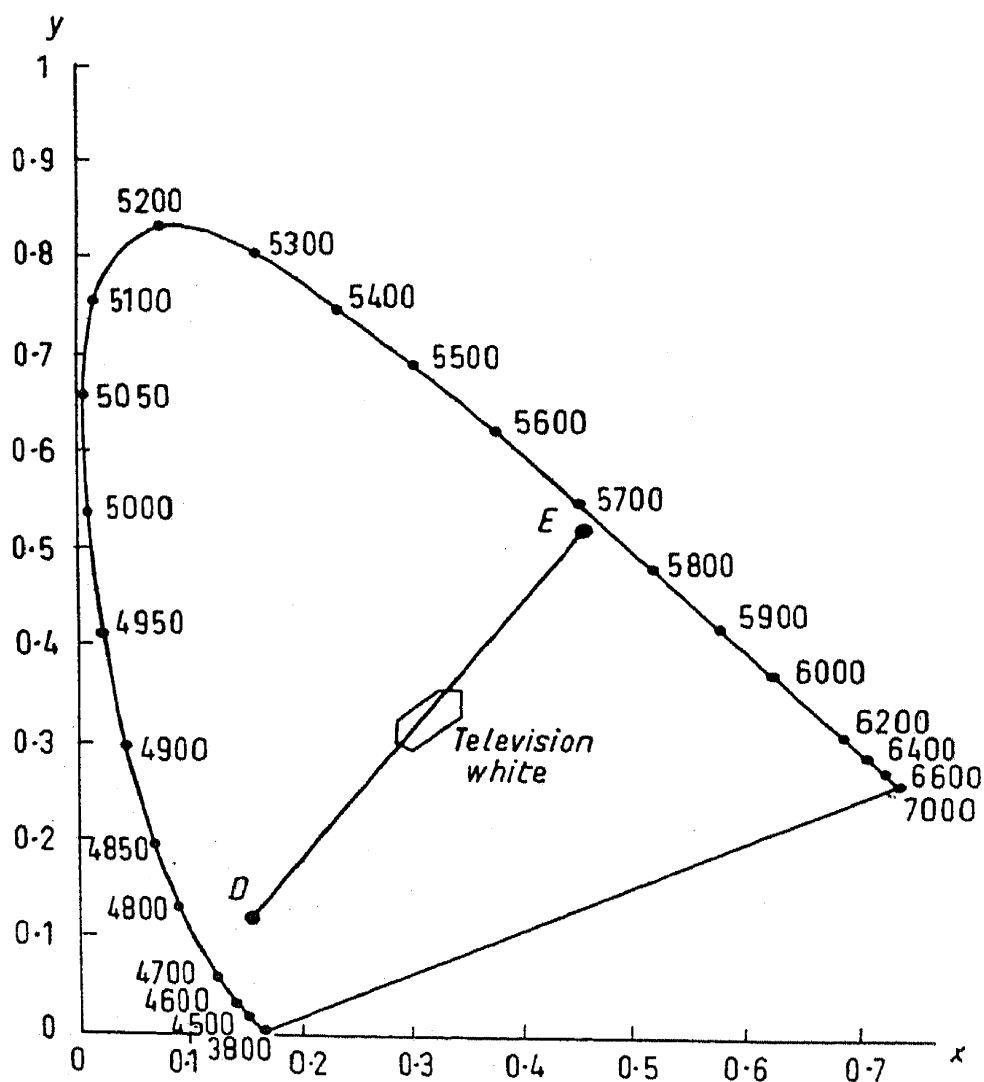
Fig. X.14 *Additive mixture of colours D and E*

D *Blue phosphor* $(Ca, Mg)SiO_3-Ti$

E *Yellow phosphor* $(0.855 \ Zn, \ 0.12 \ Be, \ 0.025 \ Mn)_2SiO_4$

(Kröger, Bril and Dikhoff)

dominantly a green band, have about the same *dominant wavelength*, but the purities are quite different.†
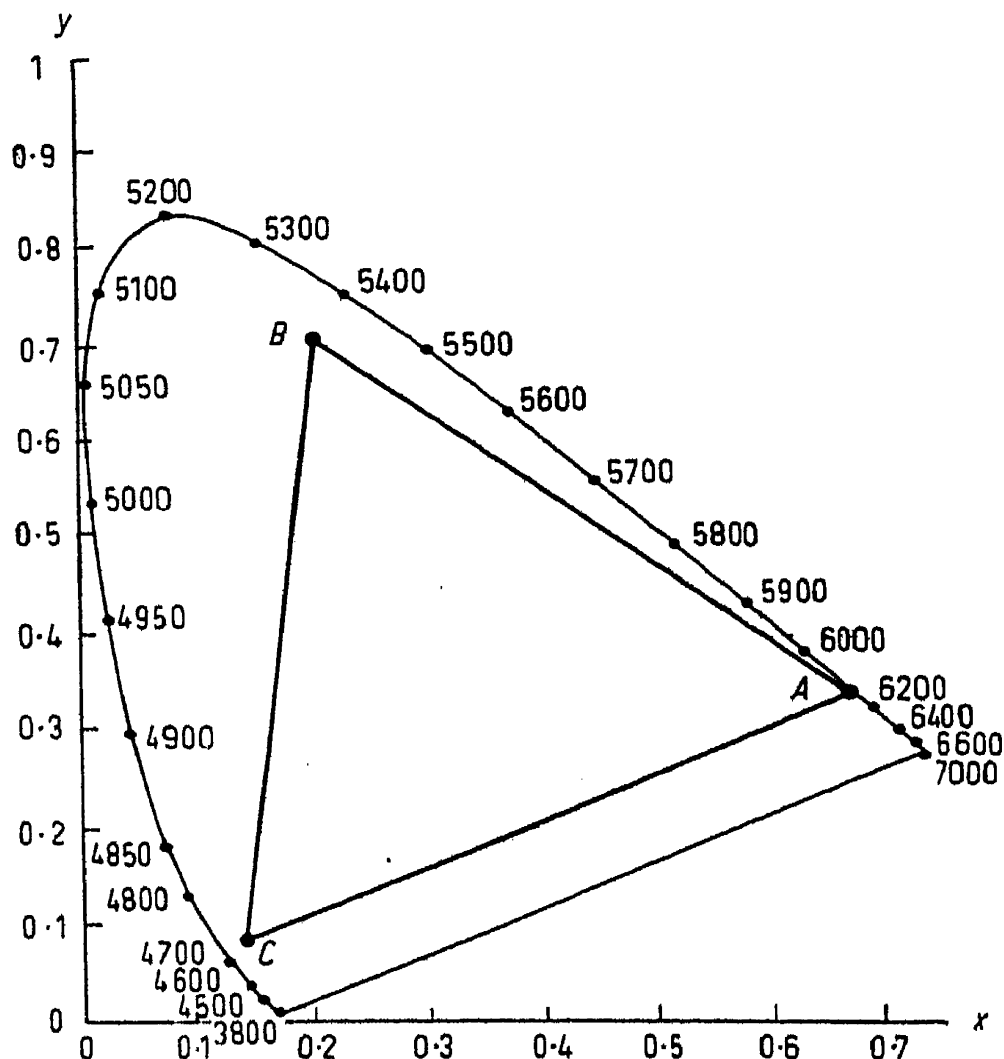
Fig. X.15 *The Maxwell colour triangle used for colour television assessment*

A *Red phosphor*
B *Green phosphor*
C *Blue phosphor*

† Leverenz gives in his book the colour diagram locations of ZnS+CdS with copper and silver activators. A remarkable application of such a diagram is to be found in the work of Kröger, Bril and Dikhoff (1952), who show that a white colour cannot be obtained with a mixed ZnS–CdS–Ag–Cu phosphor, whatever the relative proportions of constituents. In contrast, this can also be achieved with a mixture (0·86 Zn, 0·14 Cd)S(5×10⁻⁵ Ag, 5×10⁻⁵ Au, 3×10⁻⁴ Al). It is also worth noting in the diagrams given by Kröger, Bril and Dikhoff that the point for ZnS(Cu) (blende form) is almost superposed on the point for (0·97Zn, 0·03 Cd)S–Cu (wurtzite). This shows that a change in colour in passing from wurtzite to blende can also be obtained by reducing the energy gap for wurtzite (cf. page 115).

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2. *Two-colour mixtures: monochrome cathode-ray tube screens* (*black and white*)

The colours obtained by addition of two colours D and E are represented by the points of the segment DE. A suitably chosen mixture of two phosphors can thus give white. A blue- and a yellow-emitting phosphor can be used such as ZnS(Ag) (blue) and (0·61 Zn, 0·39 Cd)S–Ag (yellow), or

$$(Ca, Mg)SiO_3\text{–Ti (blue)}$$

and $\quad (0.855 \text{ Zn}, 0.12 \text{ Be})_2SiO_4\text{–Mn (yellow)}$

3. *Three-colour mixtures: colour television*

Additive superposition of the three colours A, B and C can give a point anywhere within the triangle ABC, but using phosphors like this cannot give points outside the triangle. The loss of information resulting from this has been calculated (12 per cent) and it has been shown to be less than that in the usual colour mixing in printing processes (30 per cent).

The choice thus provided by the three summits of the Maxwell triangle is

$$\text{Red phosphor } A \quad \begin{cases} x = 0.67 \\ y = 0.33 \end{cases}$$

$$\text{Green phosphor } B \begin{cases} x = 0.21 \\ y = 0.71 \end{cases}$$

$$\text{Blue phosphor } C \quad \begin{cases} x = 0.14 \\ y = 0.08 \end{cases}$$

The most difficult to obtain is the red phosphor.

TABLE X.5

Some phosphors used for colour television (Klasens and Bril)

		x	y
Red	ZnSe(Cu)	0·66	0·34
	(0·20 Zn, 0·80 Cd)S(Ag)	0·67	0·33
	(0·97 Zn, 0·03 Cd)Se(Cu)	0·67	0·33
	$Zn_3(PO_4)_2(Mn)$	0·67	0·33
Green	$Zn_2SiO_4(Mn)$	0·20	0·72
Blue	ZnS(Ag) blende	0·15	0·05
	wurtzite	0·15	0·03
	$(Ca, Mg)SiO_3(Ti)$	0·16	0·13

Different techniques for obtaining good colour have been proposed. The best result is obtained by using three separate tubes with

red, green and blue screens respectively and a system for superposing the images in projection. The cost of this method is rather high. The R.C.A. system uses a spot pattern of three different coloured phosphors, each colour receiving only the electron beam signal appropriate to it. At a sufficient distance the mosaicity of the screen is not apparent.

APPENDIX II

Relation between photometric units of luminescence†

1 candle/cm^2 = 1 stilb = π lamberts = 2,919 foot lamberts
$= \pi$ lumens emitted per cm^2 of a surface obeying Lambert's law

1 millilambert = 10^{-3} lumen emitted per cm^2 of a surface obeying Lambert's law
= 0·929 foot lambert
= 10 effective lux or apostilbs or blondels

1 watt = 685 lumens = $6·28 \times 10^{18}$ eV/sec = $2·83 \times 10^{18}$ photons/ sec for complete power conversion of photons of 2·22 eV energy (maximum eye sensitivity is a $\lambda = 5,560$ Å equivalent to 2·22 eV)

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